## ROLE OF IONIC LIQUIDS ON THE REACTIVITY AND SELECTIVITY OF DIELS-ALDER REACTIONS AND SINGLE SITE CATALYSTS

by

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#### ABSTRACT

# ROLE OF IONIC LIQUIDS ON THE REACTIVITY AND SELECTIVITY OF DIELS-ALDER REACTIONS AND SINGLE SITE CATALYSTS

Ionic liquids (ILs) have gained interest because of their features such as high thermal stability, high chemical inertness, conductivity, their ability to dissolve organic and inorganic substances. It is possible to tune these properties offering advantages for a wide range of applications namely solutions, synthesis and catalysis. In this thesis, the solvent and ligand effects of ILs are investigated in the case of organic reactions and single-site catalysts (SACs) by using Density Functional Theory (DFT). Then, the influence of electron-donor/acceptor properties of the SACs on the catalytic activities and stabilities of Ir/Rh including complexes are examined by means of computational tools. Firstly, the role of ILs as solvents in the Diels-Alder reactions is modeled. The fact that ILs can have hydrogen bonding interactions with the dienophiles, and thus significantly affect the endo selectivity and the rate of the Diels-Alder reactions has been assessed. The atomically dispersed catalysts in the presence of SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- and MgO supported-Ir(CO)<sub>2</sub> complexes are analyzed in order to understand the support effects on the electronic properties of the active sites and stabilities of the catalysts. Chapter 5 deals with the electron-donor/acceptor properties of ILs by using IL coated/uncoated MgO supported Ir(CO)<sub>2</sub> complexes in the presence of [Bmim][OAc] and [Bmim][PF<sub>6</sub>]. In order to understand the ligand effects on the catalytic properties of the SACs, ligand modification reactions between carbonyl and acetylene groups in the case of zeolite-supported Rh(CO)<sub>2</sub> complexes are modeled by considering the proton mobility. Finally, the hydrogenation reaction mechanisms for 1,3-butadiene over  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex is studied and the reasons behind the 1-butene selectivity have been clarified. Overall, this study contributes to a better understanding of the solvent and ligand effects of ILs on the chemical reactions and the catalytic systems.

### ÖZET

# DIELS-ALDER REAKSİYONLARININ VE TEK ATOM MERKEZLİ KATALİZÖRLERİN REAKTİVİTE VE SEÇİCİLİKLERİ ÜZERİNE İYONİK SIVILARIN ROLÜ

İyonik sıvılar (IL'ler), yüksek termal kararlılık, yüksek kimyasal inertlik, iletkenlik, organik ve inorganik maddeleri çözme yetenekleri gibi özelliklerinden dolayı ilgi görmüştür. Çözücü, sentez ve kataliz gibi çok çeşitli uygulamalar için avantajlar sunan bu özellikleri ayarlamak mümkündür. Bu tezde, IL'lerin solvent ve ligand etkileri, organik reaksiyonlar ve tek bölgeli katalizörler (SAC'ler) durumunda Yoğunluk Fonksiyonel Teorisi (YFT) kullanılarak araştırılmıştır. Daha sonra, SAC'lerin elektron verici/alıcı özelliklerinin, Ir/Rh içeren komplekslerin katalitik aktiviteleri ve stabiliteleri üzerindeki etkisi, hesaplama araçları vasıtasıyla incelenmiştir. İlk olarak, Diels-Alder reaksiyonlarında çözücü olarak IL'lerin rolü modellenmiştir. IL'lerin dienofillerle hidrojen bağı etkileşimlerine sahip olabileceği ve bu nedenle endo seçiciliği ve Diels-Alder reaksiyonlarının hızını önemli ölçüde etkilediği gerçeği değerlendirilmiştir. Aktif bölgelerin elektronik özellikleri ve katalizörlerin kararlılıkları üzerindeki etkilerini anlamak için SiO<sub>2</sub>, γ-Al<sub>2</sub>O<sub>3</sub> ve MgO destekli-Ir(CO)<sub>2</sub> komplekslerinin varlığında atomik olarak dağılmış katalizörler analiz edilmiştir. Bu çalışma sonrasında, [Bmim][OAc] ve [Bmim][PF<sub>6</sub>] varlığında IL kaplı/kaplanmamış MgO destekli Ir(CO)<sub>2</sub> kompleksler kullanılarak IL'lerin elektron verici/alıcı özellikleri ele alınmıştır. Tek bölgeli katalizörlerin katalitik özellikleri üzerindeki ligand etkilerini anlamak için, zeolit destekli Rh(CO)<sub>2</sub> kompleksleri durumunda karbonil ve asetilen grupları arasındaki ligand modifikasyon reaksiyonları, proton hareketliliği dikkate alınarak modellenmiştir. Son olarak,  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> destekli Ir(CO)<sub>2</sub> kompleksi üzerinde 1,3-BD hidrojenasyon reaksiyon mekanizması incelenmiş ve 1-büten seçiciliğindeki nedenler açıklığa kavuşturulmuştur. Genel olarak, bu çalışma IL'lerin kimyasal reaksiyonlar ve katalitik sistemler üzerindeki solvent ve ligand etkilerinin daha iyi anlaşılmasına katkıda bulunacaktır.

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# LIST OF SYMBOLS

r <sub>B</sub>	Boltzman distribution ratio
r <sub>N</sub>	Endo ratio
r <sub>X</sub>	Exo ratio
r <sub>exp</sub>	Experimental ratio
eV	Electron Volt
0	Degree
Å	Angstrom
$\Delta G^{\ddagger}$	Gibbs free energy of activation
$\Delta G_{\rm rxn}$	Gibbs free energy of reaction
δ	Surface Tension
ε	Dielectric constant
μ	Dipole moment
ψ	Wave function

## LIST OF ACRONYMS/ABBREVIATIONS

B3LYP	Becke 3-Parameter, Lee, Yang and Parr functional
СР	Cyclopentadiene
CM5	Charge Model 5
ILs	Ionic Liquids
IR	Infrared
IRC	Intrinsic Reaction Coordinate
M06-2X	Hybrid meta exchange-correlation functional
NPA	Natural Population Analysis
PBE	Perdew-Burke-Ernzerhof
PES	Potential Energy Surface
RTILs	Room Temperature Ionic Liquids
r <sub>B</sub>	Boltzmann ratio
SMD	Solvation Model Based on Density
SAC	Single Atom catalysis
TS	Transition State

### **1. INTRODUCTION**

Ionic liquids are molten salts formed by the combination of cations and anions. Ionic liquids which turn into liquid at room temperature are known as Room Temperature Ionic Liquids (RTILs) [1]. Since the traditional solvents have more disadvantages like high toxicity, skin irritation and influencing grandwater sources, ILs have been considered as green solvents due to their physical and chemical properties [2, 3]. To prevent these negative impacts, ionic liquids can be used as both reagents and solvents [4]. In addition, they have significant role in determining thermal properties, kinetics and selectivies of the chemical reactions by acting as catalysts [5].



Figure 1.1. Some commonly used cations and anions in ionic liquids.

Ionic liquids have become a major subject for modern chemistry [6]. The earliest study related to ionic liquids (ILs) was reported in 1914 by Paul Walden [6]. He was the first to synthesize room temperature the ionic liquid ([EtNH<sub>3</sub>][NO<sub>3</sub>]). This was also the first example for a protic ionic liquid (PIL). Paul Walden was interested in the relation between molecular size and conductivity of these molten salts [6].

The range of investigations and interests in ILs began to spread with scientists. Hurley and Weir mixed 1-alkylpyridinium halides with metal halides to make solutions [7]. In addition, John Wilkes et al. introduced 1,3-dialkyl imidazolium cations into ILs for the first time. They showed that  $[C_nC_1im]Cl-AlCl_3$  salt is liquid at room temperature. Thus, these types of cations ( $[C_nC_1im]^+$ ) became most popular for making ILs. They also reported that the acidic protons of the imidazolium rings can act as hydrogen bond donors in the case of encountering strong hydrogen bond acceptors [8]. Furthermore, ILs interact with materials through hydrogen bonds. They are also known to be used as solvents and catalysts in the Freidel-Crafts reactions [9].

#### **1.1.** Applications

Hussey et al. focused on the chloro aluminate species in the ILs [8]. They claimed that the solutions of these types of ILs are superacidic and become of great importance for the application of the ILs in the oil-refining industry [8]. Another application depending on the physical properties of ionic liquids rather than their chemistry is lubricants. ILs were first reported as high performance lubricants to replace other synthetic oils by Ye et al [10]. in 2001. ILs have also the potential for generation and storage energy. They can be used as battery electrolytes. As a result, good discharge ability, non-flammability properties of ionic liquids facilitate their use in electrochemistry [11, 12]. Catalysis has an important role for chemical and biological events, academic researches and industry. There are many products such as fuels, polymers and drugs synthesized with catalytic steps. Thus, scientists try to improve new techniques to increase the performance of a catalyst with respect to activity, selectivity, cost and efficiency [13].

Catalysts can be classified as homogeneous and heterogeneous species according to relations between them and reactants phases. In homogeneous catalysis, reactants and catalyst are in the same phase, whereas their phases are different in the heterogenous catalysis. Many homogeneous catalysts are formed from transition metal atoms or clusters including a few atoms and are stabilized by suitable ligands. The properties of catalysts can be modified by changing the ligand. Thus, the morphology of the cluster provides active sites to be used effectively and makes them easy to identify [13].

Homogeneous catalysts have both high activity and selectivity. The main issue for this type of the system is to separate the catalysts from the raw materials. This results in limited applications in industry. Heterogeneous catalysts are less reactive and selective than homogeneous ones, they are more stable and separated from the reaction media easily. Hence, heterogeneous catalysts are more applicable than the other not only in the industrial applications but also in scientific researches [13].

Heterogenization of homogeneous catalyst has gained attention since the last decades in order to increase the advantages of two catalysts. This process has been performed by attaching a homogeneous catalysts to a solid support via several physical or chemical interactions. The alternative way for the heterogenization of homogeneous catalyst is known as single-site catalysts (SACs). In this way the catalyst contains only isolated atoms dispersed on a support. This dispersion on a support provides well-defined active sites. In addition, it increases the activity and the selectivity of many reactions and makes them behave like homogeneous catalysts because of their structure and catalytic performance. The SACs term was first used in 2011 by Prof. Zhang Tao and co-workers [14]. It has also been accepted by scientists dealing with catalysis in recent years [13].

In this thesis, the aim is to understand solvent effects, selectivities and catalytic behaviors of ILs in chemical reactions by performing DFT calculations.

### 2. OBJECTIVE AND SCOPE

The electronic properties of ionic liquids allow them to be used in a wide range of fields in chemistry. They can be used as environmentally friendly solvents in chemical reactions not only because of their low vapor pressure, but also because of having the ability to act as catalysts. Therefore, regulations and then their combinations in the chemical events are among the critical issues for the scientist. Theoretical calculations and simulations are clearly important in order to understand these subjects. In the present work, we want to explain the behaviour of ionic liquids influencing chemical reactions and catalytic systems by using computational tools.

Single site catalysis has become a crucial issue for energy and environmental science. Until now, it has been developed by trial-and-error experimentally. The design of a catalyst being one of the most important goals for the scientists computational tools have started to be employed in this area. For this purpose, DFT is a convenient modelling method to investigate the rational or real model for the single site catalysts. DFT calculations have been widely performed to understand the catalytic system. Although there are numerous experimental studies for understanding the effects of catalysts on the electronic structure of the metal oxide supported  $Ir(CO)_2$  complexes, DFT calculations are limited. Therefore, we will conduct DFT calculations to find real models for the IL and the metal oxide supported complex couple to explain electronic behavior of the active site in the complexes of interest and will get deeper insight into the nature of the interactions between ILs and single site catalysts.

Brief informations about the ILs, SACs and their applications are provided in the introduction part of the dissertation. More detailed discussions about to their importance, effects and usages are given in the following chapters.

In Chapter 3, the effects of ionic liquids on reactivity and selectivity of the Diels-Alder reactions will be discussed. Furthermore, detailed explanations on the interactions of ionic liquids with reaction media and appropriate methodology will be presented in the relevant section. In the last years, ionic liquids have been used as substitutes to common solvents since they combine good solubility properties with small vapor pressures. Herein, the Diels-Alder reactions of CP with acrolein, methyl acrylate and acrylonitrile in ionic liquids ( $[Emim][N(Tf)_2]$ ), ( $[Hbim][N(Tf)_2]$  and ([Bmim][OTf]) have been modeled with density functional theory to explore the effect of ionic liquids on the endo selectivity in the adducts. Besides the hydrogen bonding interactions between the cation and the diene in all the structures, endo transition structures are slightly better stabilized than exo transition structures because of the favorable interactions between the H's of the CP ring and the O's of the  $[N(Tf)_2]^-$  and  $[OTf]^-$  anions of the IL's. In this study, B3LYP/6-31+G(d) and M06-2X/6-31+G\* calculations have demonstrated that endo selectivity in the Diels-Alder reactions can be achieved in the presence of ionic liquids in agreement with experiments.

In Chapter 4, catalysis is a scientific discipline dealing not only with the mechanisms of catalytic reactions but also with the preparation, properties and applications of different catalysts. Several academic and industrial institutes focus on the studies related to catalysis and also developments of new catalysts. In metal oxide supported catalysis, a metal ion interacts with a metal oxide support. The metallic active sites in the metal oxide supported catalysts have key roles in the catalytic systems. Thus, the kind of metal used in the support has a crucial role to determine the effects of supports on these properties. Metal oxide supports have important effects on the active sites, since they lead to novel electronic properties. These electronic properties can make significant contributions to the physical and chemical behaviors of the active sites. Based on both experimental and computational findings mentioned in this work, it is possible to increase the catalytic activities and stabilises of iridium complexes by anchoring the complexes with metal oxide supports, CO and C<sub>2</sub>H<sub>4</sub> ligands. The stabilities of the metal oxide supported iridium complexes depend on the electron donor/acceptor properties of the ligands. When the ligands have strong electron-donor ability, the metal oxide supported iridium complexes are highly stable. To infer the variations on electron densities on the active sites of the metal oxide supported iridium complexes, the IR fingerprints of CO ligands attached to the iridium atoms in the complexes can be employed, since the CO bond positions of the  $Ir(CO)_2$  complexes on different supports are measures of the electron densities on the active sites in the metal oxide supported iridium complexes. In addition, appropriate morphology and methodology are required to explain the effects of

metal oxide supports in the SACs. In this part of the thesis, the electronic environment and electron donor/acceptor properties of the active sites of the  $Ir(CO)_2$  complexes will be modified by using computational tools in the presence of different metal oxide supports such as  $SiO_2$ ,  $-Al_2O_3$  and MgO.

In Chapter 5, recently, ionic liquids (ILs) have been used as ligands for single-site Ir(CO)<sub>2</sub> complexes bound to metaloxide supports because of their electron-donor/acceptor capacities. The combined effects of supports and ILs as ligands may pave the way to the tuning of the surrounding electronic properties to increase electron-donor/acceptor efficiency in metal-oxide supported Ir(CO)<sub>2</sub> complexes. Herein, we have used Density Functional Theory to model Ir(CO)<sub>2</sub> complexes bound to MgO supports with and without the presence of an IL to explain the role of ILs in modifying the electronic structure of the supported complex. Comparison of the v(CO) band stretching frequencies with experimental results has led to the rationalization of the factors driving the interactions between the IL, the support, and the catalyst as well as the justification of the methodology for further studies. In this chapter, different arrangements between ionic liquid (IL) and metal oxide supported Ir(CO)<sub>2</sub> complexes have been discussed. These arrangements can have anion-catalyst, cationanion-catalyst or cation-catalyst-anion sequences. There are many experimental studies to understand effects of ILs on the metal oxide supported Ir(CO)<sub>2</sub> complexes but there are limited computational works to explain the real model including the three components. In this part of the dissertation, several orientations among the MgO metal oxide supported Ir(CO)<sub>2</sub> catalyst and ionic liquids such as [Bmim][OAc] and [Bmim][PF<sub>6</sub>] will be introduced to find the best model for the metal oxide supported complex and ionic liquid couple and to understand the importance of ionic liquids for the catalytic systems.

In Chapter 6, zeolites are useful catalysts for chemical reactions including organic compounds. Zeolites can promote acid-base reactions. Zeolites can also act as acid catalysts and serve as active metals or reagents. Because of the acid properties of zeolites, the proton on the zeolites can migrate from one side to another side in the catalytic system. This migration can help to increase catalytic activities of the solid catalysts. Therfore, the protonation reaction mechanism needs to be searched to understand the effects of the protonation on the chemical reactions. In addition, the chemical activities of the atomically dispersed catalysts

such as zeolites depend on the nuclearity of the metal precursor and the types of ligand. The types of the ligand bonded to the active site of the catalyst can be changed by ligand modification reactions. For this purpose, In this chapter, we want to modelize both proton mobility reactions and ligand replacement reactions between acetylene and CO groups in the case of  $Rh(CO)_2$  complexes to figure out the effects of the proton migrations on the ligand exchange reactions and suggest convenient reaction mechanism for these kinds reactions on the zeolite supported- $Rh(CO)_2$  complexes.

In Chapter 7, the hydrogenation of unsatured hydrocarbons plays key role in industrial processes. atomically dispersed catalysts (SACs) have shown excellent performance toward the selective hydrogenation of 1,3-butadiene, since they offer several advantages. First, SACs can undergo identical interactions with the reactant molecules. Second, SACs with welldefined structures ensure an ideal platform for investigation of the reaction fundamentals. Finally, the catalytic activities and electronic properties of the SACs can be altered according to the reaction media by modifying the environment of the active sites in the catalysts. Thus, these large-scale benefits motivate both academic and industrial efforts to increase the modelling and synthesis of SACs. Selective hydrogenation reactions of unsaturated hydrocarbons over metal oxide-supported transition metals like palladium, platinum, rhodium, or iridium complex are common processes, but understanding the reaction mechanisms is still challenging, since the interactions between the reactant and catalyst remain unclear. The investigations of the convenient reaction mechanisms for the hydrogenation of these substances are of current interests and theoretical calculations provide invaluable information. Therefore, the possible reaction mechanisms for the 1,3-butadiene hydrogenation will be evaluated in terms of DFT calculations to determine an appropriate reaction mechanism for these types of saturations. Herein, we have modeled the 1,3-butadiene hydrogenation mechanism in the presence of  $-Al_2O_3$  supported  $[Ir(CO)(C_4H_6)]^+$  complex using density functional theory (DFT) to elucidate the origin of the selectivity and reactivity and to suggest a reaction mechanism for the reduction reactions of butadiene to butenes and butane.

# 3. ROLE OF IONIC LIQUIDS ON THE SELECTIVITY AND THE RATE OF ORGANIC REACTIONS

#### **3.1. Introduction**

The Diels-Alder reaction is one of the most common carbon-carbon bond forming reactions used to prepare cyclic compounds in organic chemistry (Figure 3.1) [15]. This makes it a key step in the synthesis of many natural and pharmaceutical products [16-18] and has been widely studied. One of the most interesting aspects of this reaction is, its known solvent dependency which enhances reactivity and selectivity [19]. Therefore, choosing an appropriate solvent for an organic reaction is an important task. Although water is a good solvent due to its nontoxicity, most organic adducts are not soluble in water, so water has been replaced with ionic liquids [20]. On the other hand, global warming and diminishing fossil fuels require sustainable energy. One of the ways to overcome these problems is to use ionic liquids as solvents in organic reactions [21–26]. Although several ionic liquids are available, for the past few years 1,3-dialkylimidazolium ionic liquids have been employed as recyclable media in a majority of environmentally friendly reactions as opposed to limited use of hazardous chemicals [27–34]. The first ever ionic liquid mediated Diels-Alder reaction was reported by Jaeger and Tucker in 1989 [35]. This study proved remarkable rate enhancements and endo selectivity for the Diels-Alder reaction when compared with the reaction conducted in water medium. Thus in Diels-Alder reactions, ionic liquids (IL) can act as potential media [36].

The Diels-Alder reaction continues to be an important subject for both computational and experimental studies, especially solvent effects on the selectivity and rate of the reactions have gained much attention. There have been several experimental studies for the Diels-Alder reactions between cyclopentadiene and dienophiles in the presence of ILs, to understand the effect of ILs in accelerating the rate and changing the endo/exo selectivity of the reactions [37–43]. Ionic liquids are salts which are molten below 100°C [44]. Over decades, ionic liquids have become powerful alternatives to conventional organic solvents due to having negligible vapor pressure, low flammability, high conductivity, thermal stabil-

ity and reusability. These properties render them safer and more environmentally friendly than volatile organic solvents [45].

The selectivity of Diels-Alder reactions has been examined experimentally in different solvents and ionic liquids. Welton et al. have carried out experimental studies to explain the role of water, organic solvents and ionic liquids on endo/exo selectivity in Diels-Alder reactions between cyclopentadiene and different dienophiles [15]. However, computational studies which explain the role and essence of ionic liquids on the selectivities for Diels-Alder reactions are limited. In this study, the Diels-Alder reactions between cyclopentadiene and acrylonitrile in vacuum, acetonitrile, toluene and ionic liquids have been modeled with density functional theory to explore the effects of ionic liquids on the selectivities.



Figure 3.1. Cycloaddition reaction between cyclopentadiene (CP) and dienophiles (1-3) yielding endo (n) and exo (x) cycloadducts.

#### 3.2. Computational Methodology

DFT methods have been reported to be computationally economically efficient for the incorporation of electron correlation effects to complex systems. Furthermore, DFT methods have already been shown to be useful to describe Diels-Alder reactions [46]. In this study we have used the Becke three-parameter Lee-Yang-Parr exchange functional, B3LYP [47] and M06-2X [48]. All computations were carried out with the Gaussian 09 series of programs [49]. Full geometrical optimizations and conformational searches for reactants, transition state structures, products in the presence of ionic liquids have been performed in vacuum and

in solution employing the B3LYP and the M06-2X functionals with the standard 6-31+G(d) basis set [50]. Charge analysis was conducted using full natural population analysis (NPA) [51]. NPA is an alternative to conventional Mulliken population analysis, and seems to show improved numerical stability and to better describe the electron distribution in compounds of high ionic character such as ionic liquids [52]. The Gibbs free energy values have then be used to calculate the Boltzmann population of structures at 298.15K. The Boltzmann distribution is a probability distribution which gives the probability that a system will be in a certain state as a function of the energy of that state and the temperature of the system. Boltzmann populations have been calculated according to Equations (3.1) and (3.2)

$$N_i = \frac{e^{-\Delta G_i^{\ddagger}/RT}}{\sum_{j=1}^M e^{-\Delta G_j^{\ddagger}/RT}}$$
(3.1)

$$\Delta G^{\ddagger} = \sum_{i=1}^{M} N_i \Delta G_i^{\ddagger}. \tag{3.2}$$

The enantioselectivity ratios (endo/exo) have been calculated by using Equation (3.3), which can be written as

$$\frac{r_N}{r_X} = \frac{e^{-\Delta G_{endo}^{\ddagger}/RT}}{e^{-\Delta G_{exo}^{\ddagger}/RT}}$$
(3.3)

where  $N_i$  is the probability of state i, R is the gas constant, T is the temperature of the system and M is the number of states accessible to the system [53, 54]. The Boltzmann distribution has been used to calculate an average activation Gibbs free energy since there is a distribution of transition structures having Gibbs free energies very close to each other.

Solvent calculations for acetonitrile ( $\varepsilon$ = 36.64) and toluene ( $\varepsilon$ = 2.38) were performed with the SMD model [55]. We used the ideal gas approximation at T = 298.15 K and 1 atm for vacuum calculations. Because the necessary solvent parameters are not available for a [Emim][N(Tf)<sub>2</sub>] and [Hbim][N(Tf)<sub>2</sub>] we have carried out solvent calculations with the SMD continuum universal solvation model [56] for the Diels Alder reaction with explicit [Bmim][OTf] in solution of [Bmim][OTf].

#### 3.3. Results and Discussion

The Diels-Alder reaction can be stereospecific based on the relative orientation of the dienophile in the cycloadduct. For CP chosen as an adduct, stereoisomeric products resulting from whether the R group lies under (endo/n) or away from the diene (exo/x) in the transition states will be formed. In this work, we have considered the Diels-Alder reactions between cyclopentadiene (CP) and three dienophiles as acrolein (1), methyl acrylate (2) and acrylonitrile (3) to examine the selectivities of the cycloaddition reactions in the gaseous phase, in solution and in ionic liquids such as [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>] and [Bmim][OTf] (Figure 3.1 and Figure 3.2).



Figure 3.2. Structures of reactants (CP and 1-3) in the Diels-Alder reactions optimized with B3LYP/6-31+G(d) in vacuum.

In the transition state structures in vacuum, C-C distances are 2.05 Å and 2.51 Å between CP and 1 (Figure 3.3), 2.04 Å and 2.52 Å for 2 (Figure 3.4) ; 2.05 Å and 2.49 Å for 3 (Figure 3.5). As the polarity of the solvent increases, the short bond gets slightly shorter; the long bond elongates (Figures 3.3 - 3.5). The electron withdrawing groups on the dienophiles render the ethylenic carbon less rich in electron than its neighbor and as a result shorter critical distances in the transition states.







TS-1-x



TS-1-a-n



TS-1-a-x



Figure 3.3. Structures of endo(n)/exo(x) transition states for Diels-Alder reaction between CP and acrolein (1) (B3LYP/6-31+G(d) in vacuum, acetonitrile (a) and toluene (t)).



Figure 3.4. Structures of endo(n)/exo(x) transition states for Diels-Alder reaction between CP and methyl acrylate (2) (B3LYP/6-31+G(d) in vacuum, acetonitrile (a) and toluene (t)).





TS-3-x



TS-3-t-n

TS-3-t-x

Figure 3.5. Structures of endo(n)/exo(x) transition states for Diels-Alder reaction between CP and acrylonitrile (3) (B3LYP/6-31+G(d) in vacuum, acetonitrile (a) and toluene (t)).

### 3.3.1. Structures of Ionic Liquids

It is known that hydrogen bonds prevail among the cation and the anion in ionic liquids [57]. Several orientations have been chosen as initial structures for [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>] and [Bmim][OTf] based on the NPA charges on the atoms of interest. In the case of [Emim] and [Bmim], H's on C1 and C3 and the H's of CH<sub>3</sub> group bear the large positive charges and are supposed to be attacked by the anions  $[N(Tf)_2]^-$  and  $[OTf]^-$ . In the case of  $[\text{Emim}][N(\text{Tf})_2]$ , the attack can be either from the N-C-N or the -C=C- sides of the cation. It turns out that the largest number of hydrogen bonds between the anion and the cation exists when the H's on the N-C-N fragment face the [N(Tf)<sub>2</sub>] moiety (Figure 3.7) and this structure is by far more stable (7.8 kcal/mol) than the one where the H's on C3 and C4 face the anion. In the case of [Hbim], the H on C2 bears the largest positive charge and it is expected to face the most negatively charged atom in the anion (Figure 3.6); in addition to the hydrogen bond interaction with H on CH<sub>3</sub> group, the structure where H on CH<sub>3</sub> interacts with the anion turns out to be the most stable one since in this structure the O atoms of the anion can be further stabilized by the other hydrogens of the cation (Figure 3.8). In [Bmim], H's on CH<sub>3</sub> and H on C3 have the largest positive charges and are assumed to be attacked by [OTf] (Figure 3.6). When the anion [OTf] attacks from top, the complex is 9.1 kcal/mol more stable than the one where attack is from the-C=C- site (Figure 3.9). Overall, the most stable structures for [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>] and [Bmim][OTf] are displayed in Figure 3.10, having H bonding interactions between the H's on the cations and N and O's in the anions. Another remark about the global minima of the ionic liquids [Emim][N(Tf)<sub>2</sub>] and [Hbim][N(Tf)<sub>2</sub>] is about the fact that the CF<sub>3</sub> groups point in opposite directions to minimize the dipole moment of these species.

#### 3.3.2. Ionic Liquids and Dienophiles

In order to assess the role of the ionic liquids in the Diels-Alder reactions we have assumed that there is an interaction between the dienophile and the ionic liquids prior to the cycloaddition. The complexes which belong to the global minima are displayed in Figure 3.10. In the case of  $[\text{Emim}][N(\text{Tf})_2]$  and 1, the hydrogen bonds are formed between the carbonyl oxygen of acrolein and the H's of CH<sub>3</sub> group of the cation (2.26 Å and 2.76 Å). In the case of
[Hbim][N(Tf)<sub>2</sub>], besides the carbonyl oxygen (2.11 Å) there is also a stabilizing interaction between the anion and the hydrogen of the carbonyl group (2.27 Å). As in [Hbim][N(Tf)<sub>2</sub>], [Bmim][OTf] have two stabilizing interactions, H bonding between the carbonyl oxygen of the 1 and the H's of the CH<sub>3</sub> group (2.39 Å - 2.75 Å) and also between O of the anion and H of 1 (2.28 Å). For the dienophile 2, the interactions are similar in [Emim][N(Tf)<sub>2</sub>] (2.26 Å and 2.69 Å), [Hbim][N(Tf)<sub>2</sub>] (2.19 Å and 2.72 Å) and [Bmim][OTf] (2.41 Å, 2.74 Å and 2.56 Å) (Figure 3.11). Finally, for the complexes formed with acrylonitrile (3) the relevant distances are 2.34 Å and 2.53 Å in [Emim][N(Tf)<sub>2</sub>], 2.48 Å, 2.83 Å in [Hbim][N(Tf)<sub>2</sub>] and 2.37 Å in [Bmim][OTf] (Figure 3.11).



Figure 3.6. Charge distribution of (a) cations and (b) anions in the ionic liquids.



Figure 3.7. 3D structures and relative Gibbs free energies for [Emim][N(Tf)<sub>2</sub>], (B3LYP/6-31+G(d) in vacuum).



Figure 3.8. 3D structures and relative Gibbs free energies for [Hbim][N(Tf)<sub>2</sub>], (B3LYP/6-31+G(d) in vacuum).



Figure 3.9. 3D structures and relative Gibbs free energies for [Bmim][O(Tf)], (B3LYP/6-31+G(d) in vacuum).



Figure 3.10. Ionic liquids and their complexes with acrolein (1) and their dipole moments  $(\mu)$  (B3LYP/6-31+G(d)).



Figure 3.11. Ionic liquids and their complexes with methyl acrylate (2) and acrylonitrile (3) and their dipole moments ( $\mu$ ) (B3LYP/6-31+G(d) in [Hbim][N(Tf)<sub>2</sub>], [Emim][N(Tf)<sub>2</sub>] and [Bmim][OTf]).

## **3.3.3. Reaction Profiles in Ionic liquids**

<u>3.3.3.1. CP + 1</u>. The analysis of our computational results for the transition structures and the products has shown that in the case of 1, the carbonyl oxygen of acrolein is hydrogen bonded to the cationic part of the ionic liquid. Note that in the case of the adduct for  $[\text{Emim}][N(\text{Tf})_2]$ , the hydrogen bonds (2.21 Å -2.85 Å) (Figure 3.12, Figure A.1) are between the carbonyl oxygen and the H's on C4 and C5 of the cation, in the transition states this interaction is between the carbonyl oxygen and H's on C2 and C3 (2.09 Å - 2.72 Å) (Figure 3.12, Figure A.1 and Figure 3.12, Figure A.1). The transition state structures which have the lowest Gibbs free energies (TS-1-n-Emim and TS-1-x-Emim) are further stabilized by favorable interactions between the hydrogens of CP and the O=S=O moiety of the IL's (Figure 3.13, Figure A.2).

In the case of  $[Hbim][N(Tf)_2]$  the same pattern is followed for the products (Figure 3.12, Figure A.3) and transition structures (Figure 3.13, Figure A.4) except that the H bonds are between the carbonyl oxygen of 1 and H on C3 of the cationic part of  $[Hbim][N(Tf)_2]$ . These distances vary between 2.10 Å - 2.95 Å in the products and 2.01 Å - 2.89 Å in the transition structures.

The picture is similar in the case of [Bmim][OTf] with distances varying from 2.24 Å for H bonds between the carbonyl oxygen of the dienophile and H on C3 in the products (Figure 3.12, Figure A.5). In the transition states, these interactions are between the oxygen and the H's on C2 and C3 with distances ranging from 2.25 Å to 2.53 Å (Figure 3.13, Figure A.6).



Figure 3.12. Structures of endo(n)/exo(x) products the Diels-Alder reaction between CP and acrolein (1) in [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>], [Bmim][OTf] and relative Gibbs free energies and dipole moments (μ) (B3LYP/6-31+G(d)).



Figure 3.13. Structures of endo(n)/exo(x) transition states and their relative Gibbs free energies and dipole moments ( $\mu$ ) for the Diels-Alder reaction between CP and acrolein (1) in [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>] and [Bmim][OTf] (B3LYP/6-31+G(d)).

<u>3.3.3.2. CP + 2.</u> In the products and transition states obtained from the Diels-Alder reaction of CP and 2, the hydrogen bonds are between the carbonyl oxygen of methyl acrylate and

H's of the  $CH_3$  group of Emim with distances varying from 2.21 Å - 2.96 Å in the products (Figure 3.14, Figure A.7) and 2.26 - 2.56 Å in the transition states (Figure 3.15, Figure A.8).

In the presence of  $[Hbim][N(Tf)_2]$ , one endo (P-2-n-Hbim) and one exo product (P-2-x-Hbim) and their transition states (TS-2-n-Hbim and TS-2-x-Hbim) are formed. The stabilizing interactions have distances of 2.18 and 2.19 Å (between carbonyl oxygen and the H on C3) and 2.41 and 2.74 Å (between the oxygen of anionic part and the H on C2) in the products (Figure 3.14, Figure A.9) and 2.03 and 2.04 Å (between the carbonyl oxygen and the H on C3) and 2.61 and 2.65 Å (between the anionic oxygen and H of the 2) in the transition states (Figure 3.15, Figure A.10).

In the case of CP and 2 in [Bmim][OTf] one endo (P-2-n-Bmim) and one exo products (P-2-x-Bmim) (Figure 3.14) and their transition states (TS-2-n-Bmim and TS-2-x-Bmim) (Figure 3.15) have been located. The H bond distances between the carbonyl oxygen of methyl acrylate and the H's on C4 and C5 [Bmim] vary from 2.18 Å - 2.80 Å and 2.31 Å - 2.59 Å in products and transition states, respectively.

<u>3.3.3.3. CP + 3.</u> In the case of CP and 3, H bond interactions between the nitrogen of the CN group in acrylonitrile (3) and the H's on C2 and C3 [Emim] range from 2.35 Å - 2.77 Å in the products (Figure 3.16), 2.41 - 2.81 Å in the transition states (Figure 3.17). In the case of [Hbim][N(Tf)<sub>2</sub>], hydrogen bonds are between the H's on C4 and C5 of [Hbim] and the nitrogen of the -CN group. These distances range from 2.42 Å - 2.88 Å in products (Figure 3.16) and 2.35 Å - 2.88 Å in transition states (Figure 3.17). In the presence of [Bmim][OTf], the interactions between H's of C3 and C4 on [Bmim] and N of 3 are in the range of 2.34 Å - 2.35 Å in products (Figure 3.16). In transition states, the distances for these interactions are in the range of 2.31 Å - 2.32 Å between the H on C4 of [Bmim] and the N of 3 (Figure 3.17).



Figure 3.14. Structures of endo(n)/exo(x) products for the Diels-Alder reaction between CP and methyl acrylate (2) in [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>] and [Bmim][OTf] and their relative Gibbs free energies and dipole moments (μ) (B3LYP/6-31+G(d)).



Figure 3.15. Structures of endo(n)/exo(x) transiton states for the Diels-Alder reaction between CP and methyl acrylate (2) in [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>] and [Bmim][OTf] and relative Gibbs free energies and dipole moments (μ) (B3LYP/6-31+G(d)).



Figure 3.16. Structures of endo(n)/exo(x) products for Diels-Alder reaction between CP and acrylonitrile (3) in [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>] and [Bmim][OTf] and relative Gibbs free energies and dipole moments ( $\mu$ ) (B3LYP/6-31+G(d)).



Figure 3.17. Structures of endo(n)/exo(x) transiton states for Diels-Alder reaction betweenCP and acrylonitrile (3) in [Emim][N(Tf)<sub>2</sub>], [Hbim][N(Tf)<sub>2</sub>] and [Bmim][OTf] and relativeGibbs free energies and dipole moments (μ) (B3LYP/6-31+G(d)).

Table 3.1. Endo/Exo ratios  $(r_N/r_X)$  for the Diels-Alder reactions between CP and the dienophiles in vacuum, acetonitrile and toluene

(B3LYP/6-31+G(d)).

,	rexp		I	ı	I	3.6	4.1	1.9	2.4	2.7	1.1
1	rN/rX		1.2	1.1	0.8	1.1	3.9	1.8	1.2	2.1	1.0
- <del>1-1</del> 7	J <sup>т</sup>	$\Delta G_B{}^{\ddagger}{}_X$	32.7	32.5	32.4	31.2	33.3	31.7	32.5	33.3	32.6
	70	$\Delta {\rm G}_B{}^{\sharp}{}_{\rm N}$	32.6	32.4	32.5	31.1	32.5	31.4	32.4	32.9	32.6
	rxn	$\Delta G_{ m rxnX}$	2.9	1.2	-0.7	4.6	3.4	0.7	3.9	2.3	0.1
	DD	$\Delta G_{ m rxnN}$	2.8	1.3	-0.5	4.6	2.7	0.5	3.7	2.0	0.2
Danotione	Keactions		CP+1	CP+2	CP+3	CP+1	CP+2	CP+3	CP+1	CP+2	CP+3
Danation Madia	Keaction Media		Vacuum			Acetonitrile			Toluene		

r <sub>exp</sub>		4.1	4.1	1.4	4.8	6.1	1.2	4.1	4.3	2.3
rbn/rbx		7.4	7.4	2.6	1.5	3.9	0.7	3.2	2.1	1.3
r <sub>N</sub> /r <sub>X</sub>		1.2	4.1	2.6	2.8	3.9	0.7	6.5	2.1	1.4
	$\Delta \mathrm{G}_B{}^{\ddagger}_X$	32.9	34.0	31.9	31.8	32.6	32.9	31.7	31.1	32.2
ΔG	$\Delta { m G}_B{}^{\ddagger}{ m N}$	31.6	32.8	31.3	31.5	31.8	33.1	31.0	30.7	32.1
÷.	$\Delta G^{\ddagger}_{\mathrm{X}}$	31.6	33.7	31.9	31.2	32.6	32.0	31.2	31.1	31.9
40	$\Delta G^{\ddagger}{}_{ m N}$	31.5	32.8	31.3	30.6	31.8	32.3	30.6	30.7	31.7
rxn	$\Delta G_{ m rxnX}$	2.6	2.3	0.1	3.1	1.2	0.8	3.8	1.7	0.0
ΔG	$\Delta G_{ m rxnN}$	2.6	1.8	-0.4	1.6	1.0	0.5	2.6	1.6	-0.5
Reactions		CP+1	CP+2	CP+3	CP+1	CP+2	CP+3	CP+1	CP+2	CP+3
Reaction Media		$[\text{Emim}][N(Tf)_2]$			[Hbim][N(Tf) <sub>2</sub> ]			[Bmim][OTf]		

Table 3.2. Endo/Exo ratios (r<sub>N</sub>/r<sub>X</sub>) for the Diels-Alder reactions between CP and the dienophiles in the presence of ILs (B3LYP/6-31+G(d)).

Table 3.3. Endo/Exo ratios (r<sub>N</sub>/r<sub>X</sub>) for the Diels-Alder reactions between CP and the dienophiles (1-3) with [Bmim][OTf] with/without solvent

(M06-2X/6-31+G\*).

	Reactions	Δ0	** (5	ΔC	$B^{\ddagger}$	$r_N/r_X$	r <sub>BN</sub> /r <sub>BX</sub>	$\mathbf{r}_{exp}$
		$\Delta G^{\ddagger}{}_{ m N}$	$\Delta G^{\ddagger}_{\rm X}$	$\Delta G_B^{\ddagger}{}_N$	$\Delta { m G}_B{}^{\ddagger}{ m X}$			
CP.	+1	23.9	I	25.3	I	I	ı	4.1
CP-	+2	23.5	23.7	23.5	23.7	1.4	1.4	4.3
CP-	F3	25.4	25.5	27.8	27.1	1.1	1.6	2.3
CP.	+	25.4	ı	25.4	ı	ı	I	4.1
CP	+2	23.6	24.1	23.6	24.1	2.5	2.5	4.3
CP	+3	25.7	27.4	26.2	27.3	1.0	6.1	2.3

The Gibbs free energies of reaction ( $\Delta G_{rxn}$ ) and the Gibbs free energies of activation  $(\Delta G^{\ddagger})$  reported in Table 3.1 and Table 3.2 have been evaluated in two different ways: by considering the energetics of the global minima in each case and by having a Boltzmann average of the energetics of the structures reported in the appendix. The Diels-Alder reactions considered in this study are slightly endothermic; the presence of ionic liquids does not alter this behavior. The calculated ratios in Table 3.1 and Table 3.2 reveal the fact that the endo/exo ratio is higher for the dienophiles 1, and 2 compared to 3 as can be detected in the H—O and H—N bond distances which vary between 2.01 Å to 2.30 Å in the former as compared to the 2.35 Å to 2.43 Å in the latter. In the stationary structures corresponding to global minima for the transition structures, the diene has favorable interactions with the anion, whereas the dienophile interacts favorably with the cation. In general, the H's in the proximity of the heteroatom in the cation interact with the anion and the dienophile, the diene is stabilized by interactions with the CF<sub>3</sub> group of the anion. In every case the endo transition structures are slightly better stabilized than the exo structures. The best agreement with experiment is obtained when considering the structure correponding to the global minima on the potential energy surface.

The M06-2X/6-31+G\* methodology has been used in vacuum and in a medium where [Bmim][OTf] is the continuum: the barriers are lower by 5-7 kcal.mol-1 as compared to the ones with B3LYP/ 6-31+G\* however the endo adducts are still favored (Table 3.3). Note that B3LYP/6-311+G\*// B3LYP/6-31+G(d) calculations fail to reproduce the experimental  $r_N/r_X$  ratios in some cases (Table 3.4). The following parameters have been used to carry out solvent calculations with the SMD continuum universal solvation model for the Diels Alder reaction with explicit [Bmim][OTf] in solution of [Bmim][OTf]: Dielectric constant ( $\varepsilon$ ) = 13.2 [58]; index of refraction (n) = 1.4368 [59], macroscopic surface tension ( $\delta$ ) = 34.0 [60]; fraction of non-Hydrogen atoms ( $\varphi$ ) = 0.1667; fraction of non-Hydrogen atoms that are electronegative halogen atoms ( $\psi$ ) = 0.1667; Hbond acidity = 0.263 [44]; H-bond basicity = 0.374 [56].

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B3LYP/6-311+G(d,p)/

Reaction Media	Reactions	70	÷5	ΔQ	$B^{\ddagger}$	r <sub>N</sub> /r <sub>X</sub>	r <sub>BN</sub> /r <sub>BX</sub>	rexp
		$\Delta G^{\ddagger}{}_{ m N}$	$\Delta G^{\ddagger}_{\mathbf{X}}$	$\Delta { m G}_B{}^{\ddagger}{ m N}$	$\Delta \mathrm{G}_B{}^{\ddagger}_X$			
$[\text{Emim}][N(\text{Tf})_2]$	CP+1	31.9	32.0	32.2	32.1	1.1	0.8	4.1
	CP+2	32.2	32.8	32.2	33.1	2.7	4.7	4.1
	CP+3	32.4	32.5	32.4	32.5	1.1	1.1	1.4
$[Hbim][N(Tf)_2]$	CP+1	31.3	31.5	32.4	32.5	1.0	1.3	4.8
	CP+2	32.8	33.2	32.8	33.2	2.1	2.1	6.1
	CP+3	37.7	37.8	37.9	37.8	0.9	0.8	1.2
[Bmim][OTf]	CP+1	30.7	32.0	31.5	32.4	8.7	4.5	4.1
	CP+2	31.3	31.9	31.3	31.9	2.7	2.7	4.3
	CP+3	32.4	32.5	33.2	33.1	1.4	0.9	2.3

Acevedo et al. have emphasized advantages of ionic liquids on rate and endo selectivity of the Diels-Alder reaction between cyclopentadiene and methyl acrylate in the presence of 1-ethyl-3-methylimidazolium tetrachloroaluminate [Emim][AlCl<sub>4</sub>] and 1-ethyl-3-methylimidazolium heptachlorodialuminate [Emim][Al<sub>2</sub>Cl<sub>7</sub>] [61]. The B3LYP/6-31G(d) and B3LYP/6-311+G(2d,p) methodologies have been used to find out that the most acidic imidazolium proton and ring hydrogens are towards the carbonyl oxygen of methyl acrylate and the activation Gibbs free energies (B3LYP/6-311+G(2d,p)) are 34.6 kcal/mol in vacuum, 37.5 kcal/mol in [Emim][AlCl<sub>4</sub>] and 37.6 kcal/mol in [Emim][Al<sub>2</sub>Cl<sub>7</sub>]. In this study we have calculated (B3LYP/6-31+G(d)) the Gibbs free energies to be 32.8 kcal/mol in [Emim][N(Tf)<sub>2</sub>], 31.8 kcal/mol in [Hbim][N(Tf)<sub>2</sub>] and 30.7 kcal/mol in [Bmim][OTf] (Table 3.2); our values are slightly lower than the ones calculated with the AlCl<sub>4</sub> and Al<sub>2</sub>Cl<sub>7</sub> anions.

Kumar et al. have reported the effect of solvents and their salt solutions on the rate and stereoselectivities of the Diels-Alder reactions between CP and methyl acrylate and its derivatives [62]. They used chloroaluminates in N-1-butylpyridinium chloride (BPC) or 1ethyl-3-methyl-1-H-imidazolium chloride (EMIC). They showed that the Diels-Alder reaction between CP and methyl methacrylate shows higher stereoselectivity towards the endo product in the presence of chloroaluminate ionic liquid.

In the work of Welton and co-workers, the same reaction in different media such as methanol, acetone, ethanol, diethyl ether and in the presence of [Bmim][OTf] has been discussed [63]. The endo/exo ratio for the above mentioned reaction has been found as 6.7 in methanol, 5.2 in ethanol, 4.2 in acetone, 2.9 in diethyl ether and 4.5 in [Bmim][OTf]. In the study of Evanseck et al, the Diels-Alder reaction with 1-ethyl-3-methylimidazolium chloride (EMIC) in basic ([EMI][AlCl<sub>4</sub>], acidic ([EMIC][AlCl<sub>3</sub>]) melt and water media was investigated. Free energy changes for the reaction have been calculated as 42.9 in water, 40.0 in acidic melt, 43.5 in basic melt [64].

The reaction between CP and methyl methacrylate has also been modeled (M06-2X/6-31+G(d)/B3LYP/6-31+G(d) and MP2/6-311+G(d,p)/B3LYP/6-31+G(d)) by Gangluy et al. in the presence of both [EMI]<sup>+</sup>[Cl]<sup>-</sup> and [EMI]<sup>+</sup> [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> IL ion pairs [65]. The authors attribute the stabilization of the endo adduct to the counterion of the acidic melt whose role

is claimed to be crucial in reversing the stereoselectivity from exo to endo. This finding is in agreement with this study where we mention the extra stabilization of the endo adduct via stabilization of the H atoms of the CP ring with the O=S=O groups of the anion.

## 3.4. Conclusion

We have carried out a detailed theoretical study (B3LYP/6-31+G(d)) of the Diels-Alder reactions between cyclopentadiene and methyl acrylate, acrolein and acrylonitrile with/without ionic liquid to determine the effect of solvent on the rate and selectivity of the reactions; this study has been carried out in vacuum, acetonitrile, toluene and three different ionic liquids. The H bond donation ability of the cation and the electronegative elements in the anion are important factors which render ionic liquids suitable as solvent and catalysts which enhance the setereoselectivities and reactivities. We have been able to determine the source of the selectivity and have found out that dienophiles like methyl acrylate and acrolein are better discriminated (endo/exo) because of the strength of hydrogen bonds. The ionic liquids utilized in this study seem to behave similarly in stabilizing the transition structures: there is no net preference of one over the other, it is the cation which interacts with the dienophile and the anion which stabilizes the CP ring. In general endo transition structures are slightly better stabilized than exo transition structures due the shape of the endo transition structures which allows extra stabilization between the H's of the CP ring and the O=S=O groups of the IL's.

Among the ionic liquids taken into consideration in this study,  $[Hbim][N(Tf)_2]$  seems to trigger the selectivity slightly more than the others. This behavior can be attributed to the cation which has H atoms directly in the vicinity of the heteroatom rather than the methyl groups like in  $[Emim][N(Tf)_2]$  and [Bmim][OTf].

The ionic liquids do not increase the reactivity in most cases except for [Bmim][OTf] which is not as selective as the others. This behavior may stem from the small anion which has four O atoms available for bonding with the H's of CP. Overall, the computational study carried out in this work is expected to guide experimentalists in designing new experiments with ionic liquids based on their expectations.

## 4. MODELLING THE ELECTRONIC STRUCTURE OF ATOMICALLY DISPERSED SUPPORTED IRIDIUM CATALYST

#### 4.1. Introduction

Catalysis is known as modification of the rate of a chemical reaction by addition a substance not consumed during the reaction [66, 67]. It plays an important role in chemical industry [13]. The first time a catalyst was used is in the industry in 1746 by J. Hughes for the manufacture of lead chamber sulfiric acid [68]. In reality, over 90% of all chemical products such as medicines, polymers, fuels and so on are synthesized involving catalytic reactions. Therefore, scientists want to improve the catalyst performance with respect to activity, selectivity, cost, efficiency and more [13]. Catalysts can be classified generally according to their pyhsical state, chemical nature or the kinds of reactions which they catalyze. Catalysts may be gas, liquids or solids. In homogeneous catalysis, the catalyst and reactants or products are in the same phase, whereas in heterogeneous system, their phases differ from each other [66]. It is known that acids and bases are used as homogeneous catalysts in organic synthesis. In addition, homogeneous catalysts can control molecular weight distributions and stereochemistry of the substances in polymerization reactions [69]. One of the major drawbacks of the homogeneous catalysis is the separation of starting materials from products. One possible solution to deal with this problem is to fix the molecular metal complexes on solid supports by creating organometallic centers on the surfaces of the supports. The development of these materials ensures opportunities to understand, design heterogeneous catalytsts at a molecular level and lay on a bridge between homogeneous and heterogeneous catalytic systems. The supported metal catalysts arise from combination of metal particles with broad distributions and unsteady morphology. Each metal particle has multiple active sites with different performances [70]. The main role of the support is to stabilize small metallic particles by chemical bonding and thus to provide access to a much larger number of catalytically active sites than in the corresponding bulk metal [71]. Downsizing bulk metarials in the nanoparticles on a given surface leads to heterogenous catalysts with single metal atoms on the surface. Such catalytic systems are defined as SACs. Metals such as gold, platinum, iron, aluminium, magnesium and silicon themselves and their complexes fall into the heterogeneous catalyst class. Especially, metal oxide supported heterogeneous catalysts such as  $SiO_2$ ,  $Fe_2O_3$ ,  $TiO_2$ , MgO and  $Al_2O_3$  have attracted great attention by offering new catalytic properties and also facilitating the use of expensive metals (Au, Pt etc) [72].

Adjustment of the surface area and the morphologies of the metal oxide supported nanoparticles is extremely important, since most chemical events occur on the surface of the nanoparticles. Thus, smaller particles with increased surface area have a larger number of active sites [13]. Yang et al. [70] have claimed that the size of metal particles is the most important factor determining reactivity and properties of metal supported catalysts. They have reported the relation between particle size minimization and metal surface free energy. Hence, as the particle size of metal decreases, the metal surface energy decreases and the specific activities of metal atoms in the cluster increase (Figure 4.1).



Figure 4.1. Relation between surface free energy and metal size of cluster in the metalic supported catalyst.

Another way of altering the catalytic behavior, selectivity and electronic environment of metal surface in the support is to manipulate the ligand to the surface of the metal cluster. Ligand is an ion or molecule binding to central atom to form coordination complex [10]. CO,  $C_2H_4$ , AsPh<sub>3</sub>, PEt<sub>3</sub>, PPh<sub>3</sub> and P(OPh<sub>3</sub>) are given as examples for ligands [72, 73]. Babucci and co-workers have emphasized that reactivity, selectivity and electronic properties of metal oxide supported Ir(CO)<sub>2</sub> complexes may be tuned by switching the ligand [72]. As a result, the electronic moiety, selectivity and reactivity of metal cluster depend on not only particle size of metal cluster but also on the nature of the ligand.

There has been several experimental studies for controlling stability, electronic environment and electron-donor/acceptor properties of single-site supported metal catalysts [74-80]. Kurtoğlu et al. [81] have investigated synergistic ligand effects of supports on different metal-oxide supported iridium complexes, determining how they influence the resistance of iridium to aggregation. They highlighted that the metals in the catalysts are readily reduced and sintered with marked changes in catalytic properties when they are noble. They have also reported that there are different approximations to stabilize the metals toward sintering. One possible approach is to bond them to sites which they have many coordination numbers [82]. Alternatively, different metal oxide supports or ligands, affecting on electron-donor strength of the catalyst, may be choosen to maximize the strength of the metal -support bonds [83-85]. They conducted their work by using SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO supported  $Ir(CO)_2$  and  $Ir(C_2H_4)_2$  complexes to show the effects of the supports and the ligands on the stability of the complexes and electronic environment on the iridium atom in the complexes. Their data show that resistance to sintering is favored in the the presence of strong electron-donor supports such as MgO. Density functional theory (DFT) methods have become very widely used to understand the electronic structures and properties of compounds and complexes containing transition metals [86]. Although numerous recent studies related to structure and chemical performance of these types of the metal-oxide supports are present in the literature, there is limited computational survey on describing the convenient structure affecting the electron-donor/acceptor properties, stabilities and catalytic activities of the supports. Therefore, we performed density functional theory (DFT) calculations to understand the effects of the supports and ligands on stabilities, activities and electronic properties of these complexes (Figure 4.2) in terms of (CO)<sub>sym</sub> stretching bands, bond dissociation energies (BDE) and charge distributions on iridium atoms in the complexes. The influence of the supports on the electron densities of iridium atoms in the complexes have been detected by conducting charge distributions and (CO)<sub>sym</sub> band positions calculations.

In addition, bond dissociation energies (BDE) have been calculated to show the effects of the electron densities on iridium atoms on stabilities of the  $Ir(C_2H_4)_2$  complexes with these three types of supports.



Figure 4.2. Structures considered in this study: A. Metal-oxide supported Ir(CO)<sub>2</sub> complex,B. Metal-oxide supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complex.

## 4.2. Computational Methodology

In this work, we have used the Perdew-Burke-Ernzerhof (PBE) [87] functional to optimize geometries with the 6-31G(d,p) basis set for H, C, O, Mg, Al and Si atoms and the Los Alamos National Laboratory (LANL2DZ) basis set developed by Hay and Wadt for Ir atom [88]. PBE functional has been widely used for predicting structures and energetics of the transition metal complexes [89, 90]. All calculations have been carried out with the Gaussian 09 series of programs [49]. Charge distributions have been calculated by using the Charge Model 5 (CM5) and Hirshfeld charge anaysis [91]. We used ideal gas approximation at T= 298 K and 1 atm for vacuum calculations.

## 4.3. Results and Discussion

#### 4.3.1. Metal Oxide Supported Ir(CO)<sub>2</sub> and Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> Complexes

Early experimental and computational studies have claimed that the accurate morphology of metal cluster and the interaction of the metal and the support have importance for clarifying the effects of metal oxide supports on a chemical reaction. DFT calculations can provide an alternative way to understand the structure of metal-oxide supports. However, metal clusters modeled with DFT studies may be smaller than those used experimentally in order to have reasonable computational times [92]. Therefore, for reducing the computational cost, we have modeled the metal oxide supports by reducing their sizes. In this part of the study, we have modeled  $Ir(CO)_2$  and  $Ir(C_2H_4)_2$  complexes with SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO supports (Figure 4.3 and Figure 4.4). The SiO<sub>2</sub>-supported  $Ir(CO)_2$  and  $Ir(C_2H_4)_2$  complexes were simulated by using a tetrahedral arrangement with one silicon bonded to four oxygen atoms. Vummaleti and co-workers have reported the same pattern for silicon and oxygen atoms by considering a zeolite support [93]. Biswas et al. have used  $(Al_2O_3)_n$  clusters for n = 3, 4, and 6 having a valid model for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a (110) pattern for the Al<sub>2</sub>O<sub>3</sub> surface, whereby they reported the thermodynamic stability of the bulk structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [36]. Thus, the (100) surface of the  $Al_{12}O_8$  cluster reported by Biswas et al. was used to simulate the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported Ir(CO)<sub>2</sub> and Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes [94, 95]. For MgO, the (100) crystal was used as reported in Gates et al. work [37]. In addition, the IR carbonyl stretching frequencies of the iridium dicarbonyls in the metal oxide supported-Ir(CO)<sub>2</sub> complexes have been calculated by taking into account scaling factor as 0.986 [81]. The scaled values are 2091 (2121), 2086 (2116) and 2054 (2083)  $\text{cm}^{-1}$  for the complexes (Table 4.1).

Figure 4.3 and Figure 4.4 illustrate the optimized geometries of the lowest-energy conformers obtained for SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO-supported Ir(CO)<sub>2</sub> and Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes, respectively. As described above, the SiO<sub>2</sub>-supported complexes were simulated using a tetrahedral arrangement. The crystal structure displayed for the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported complexes consists of 4, 6 and 8 membered rings. It turns out that the structure for which Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> and Ir(CO)<sub>2</sub> faces the octagonal face of the crystal is more stable and in good agreement with the experimental results than the others. For the MgO-supported complexes, the (100) crystal, where Ir atoms bond to the terrace sites through 2 Ir-O have reproduced the experimental findings [37].

Table 4.1 shows the calculated  $v(CO)_{sym}$  band positions in comparison with the experimentally detected positions. The  $v(CO)_{sym}$  bands were computationally determined as 2091, 2086, and 2054 after using a scaling factor of 0.986 [38]. Data show that the calculated  $v(CO)_{sym}$  band positions decrease in the following order of the supports: SiO<sub>2</sub> >

 $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > MgO. This order is in accordance with the order of the experimental  $v(CO)_{sym}$  band positions as tabulated in Table 4.1.

Table 4.1. Experimental and calculated band positions of  $\nu(CO)_{sym}$  for metal-oxide-supported Ir(CO)<sub>sym</sub> complexes (PBE/6-31G(d,p)).

Complexes	$v(CO)_{sym-cal}$	$v(CO)_{sym-exp}$
Ir(CO) <sub>2</sub> -SiO <sub>2</sub>	2091	2081
$Ir(CO)_2-Al_2O_3$	2086	2072
Ir(CO) <sub>2</sub> -MgO	2054	2068



Figure 4.3. Optimized structures of SiO<sub>2</sub>-,γ-Al<sub>2</sub>O<sub>3</sub>-, and MgO-supported Ir(CO)<sub>2</sub> complexes (PBE/6-31G(d,p)). Selected distances are given in Å.



Figure 4.4. Optimized structures of SiO<sub>2</sub>-, $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO-supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes (PBE/6-31G(d,p)). Selected distances are given in Å.

#### 4.3.2. Charge Analysis

Table 4.2 represents the charge analysis on Ir atoms in the  $Ir(CO)_2$  and  $Ir(C_2H_4)_2$  complexes supported on SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and MgO by using the CM5 and the Hirshfeld charge analysis. Computational data show that the charge on iridium atom decreases with an increase in the electron-donor strength of the support for both type of complexes. Thus, we infer that the electron density of the Ir atom in the supported  $Ir(C_2H_4)_2$  complexes increase in the following order of the supports: SiO<sub>2</sub> <  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> < MgO (Table 4.2). This order is

consistent with the inference derived from the corresponding v(CO) band positions of the SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO-supported Ir(CO)<sub>2</sub> complexes with the experimental positions presented in Table 4.1.

	Charge	s on Ir atoms
Sample	CM5	Hirshfeld
Ir(CO) <sub>2</sub> -SiO <sub>2</sub>	0.428	0.120
Ir(CO) <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	0.404	0.106
Ir(CO) <sub>2</sub> -MgO	0.365	0.093
$Ir(C_2H_4)_2$ -SiO <sub>2</sub>	0.479	0.204
$Ir(C_2H_4)_2-Al_2O_3$	0.456	0.181
Ir(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> -MgO	0.405	0.154

Table 4.2. Charge distributions on Ir atoms in metal oxide-supported  $Ir(CO)_2$  and  $Ir(C_2H_4)_2$  complexes (PBE/6-31G(d,p)).

## 4.3.3. Bond Dissociation Energy

The bond dissociation energy is used to quantify the strength of a chemical bond, thus, it is a measure to determine the stability of the supported Ir complexes [96]. For this purpose, bond dissociation energies were calculated for the SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO-supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes by increasing the distance between Ir and O by 0.5 Å in each step starting from the structure corresponding to global minima and taking the difference between electronic energies of the initial and final structures. This procedure was carried out for SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO-bonded to Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>, where the corresponding bond dissociation energies have been determined as 75.6, 79.5, and 98.8 kcal/mol, respectively (Table 4.3). The bond energies show the same trend as the bond distances between Ir and the O atoms on the surface (Figure 4.4 and Figure 4.5). For the SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO-supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes, the plots of electronic energies for the bond dissociations are displayed in Figure 4.6.

Kurtoğlu et al. carried out temperature-programmed reduction (TPR) experiments by flowing pure H<sub>2</sub> in to the the SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- and MgO-Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes to evaluate the influences of the supports on the resistance to aggregation of the complexes [81]. Table 4.4 displays the experimental findings [81] for the coordination number and bond distances of metal-ligand bonds in the metal oxide-supported  $Ir(C_2H_4)_2$  complexes. In the case of SiO<sub>2</sub>-, γ-Al<sub>2</sub>O<sub>3</sub>-supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes Ir-Ir coordination number is found as 6.49 and 3.66 respectively. There is no coordination evidence for the Ir-Ir atom in the presence of  $Ir(C_2H_4)_2$ -MgO complex. These results show that  $Ir(C_2H_4)_2$ -SiO<sub>2</sub> and  $Ir(C_2H_4)_2$ - $\gamma$ -Al<sub>2</sub>O<sub>3</sub> complexes undergo aggregation but the sintering or Ir clusters does not occur in the presence of the MgO-supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complex. Ir-C and Ir-O atoms represent the ligand and support interaction with the metal center. Thus, bond distances for the atoms in the SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO-supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes are also important to understand the effects of the supports on the electron densities of Ir atoms in the complexes. Thus, Ir-C bond distances were detected as 2.40 Å for SiO<sub>2</sub>-, 2.15 Å for the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- and 1.96 Å experimentally for the MgO supported  $Ir(C_2H_4)_2$  complexes. Our DFT calculations at level of PBE/6-31G(d,p) support the experimental findings. Based on the computational data shown in Table 4.3, the strengths of the support-metal-oxygen bonds associated with the dissociation energies of the complexes  $(Ir(C_2H_4)_2)$  from the surfaces of the supports increase in the order of SiO<sub>2</sub>-Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (75.6 kcal/mol)  $< \gamma$ -Al<sub>2</sub>O<sub>3</sub>- Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (79.5 kcal/mol) < MgO- $Ir(C_2H_4)_2$  (98.8 kcal/mol). As it is mentioned in 4.3.2 charge analysis part, electron donation from the support to iridium atoms increases in the order of  $SiO_2 < \gamma - Al_2O_3 < MgO$ . These results show that increasing electron donation from the support to iridium atoms results in decreasing Ir-Ir aggregation and Ir-O bond breaking. Furthermore, charge distributions and (CO)<sub>sym</sub> band positions calculations data demonstrate that iridium becomes more stable with an increase in its electron density through electron donation from the support (Table 4.1 and Table 4.2).

In summary, increasing electron donation from the support to iridium reduces the tendecy of the complexes to undergo Ir-O bond breaking and aggregation of the transition metal species.



Figure 4.5. Bond-dissociations of SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes (PBE/6-31G(d,p)).



Figure 4.6. Electronic energies of a) SiO<sub>2</sub>-, b)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and c) MgO-supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes obtained by step wise increase in Ir-O distance in each complex (PBE/6-31G(d,p)).

Sample	Bond Dissociation Energies
Ir(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> -SiO <sub>2</sub>	75.6
$Ir(C_2H_4)_2-Al_2O_3$	79.5
$Ir(C_2H_4)_2$ -MgO	98.8

Table 4.3. Bond dissociation energies (BDE) of SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes (PBE/6-31G(d,p), kcal.mol<sup>-1</sup>).

Table 4.4. Summary of experimental best-fit EXAFS parameters for the structures of SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-, and MgO-supported Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complexes.

Sample	Atoms	Coordination Number	Bond Distances (Å)
$Ir(C_2H_4)_2$ -SiO <sub>2</sub>	Ir-Ir	6.49	2.68
	Ir-C	0.87	2.40
$Ir(C_2H_4)_2-Al_2O_3$	Ir-Ir	3.66	2.75
	Ir-C	1.00	2.15
	Ir-C <sub>L</sub>	1.13	3.33
Ir(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> -MgO	Ir-O	2.19	2.06
	Ir-C	2.19	1.96

#### 4.4. Conclusion

Atomically dispersed supported  $Ir(CO)_2$  and  $Ir(C_2H_4)_2$  complexes have been modeled as catalysts on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO supports by using DFT calculations to understand the stabilities of the complexes and electron-donor/acceptor properties of the supports. The validity of the models have been tested by comparison of experimental (CO)<sub>sym</sub> band positions. PBE/6-31G(d,p) and PBE/LANL2DZ methodologies carried out in this study can be acceppted as convenient methods since the computational data obtained with these methodologies are in good agreement with experimental findings. The results reported here show that the nature of the support accounts for the differences in (CO) frequencies of the CO ligands bonded to iridium atom in the complex. These variations in the stretching bands result from the different electron-donor/acceptor properties of the supports in the complexes.

The electron-donor/acceptor properties of the supports on iridium atoms in the complexes has been discussed by performing charge analysis (CM5 and Hirshfeld). Based on the charge distribution calculations, the electron densities, corresponding to decreasing of positive charge values shown in Table 4.2, on iridium atoms in the complexes will increase in the case of employing the supports having high electron-donor properties. In this case, the Ir-C bond in the complex becomes stronger, the C-O bond strength in the CO ligand weakens and (CO)<sub>*sym*</sub> band frequency shifts to a lower value.

As a result, the catalyst has an important role for determining both the chemical and electronic properties of a substance.

# 5. INFLUENCE OF ILS ON THE ELECTRONIC ENVIRONMENT OF ATOMICALLY DISPERSED Ir ON (MgO)(100)

#### 5.1. Introduction

The importance of catalysts in the blooming of the chemical industry, as well as the development of ecologically sustainable chemical processes cannot be overlooked [97]. Metaloxide- supported catalysts have drawn wide attention because they offer new catalytic properties and also facilitate the use of metals which would be too expensive for extended industrial exploitation. Their use in important reactions such as hydrogenation and hydroformylation of olefins and methanol carbonylation is especially relevant [70,71,75,98,99]. Particularly, atomically dispersed supported metal catalysts offer the highest level of metal dispersion, hence the highest number of active sites for a given metal loading, and enable the determination of structure–performance relationships by fundamental level investigations [100]. These catalysts are exemplified by site-isolated mononuclear metal complexes, in which a metal complex is covalently bound to the support.

Control of the catalytic performance of an atomically dispersed supported metal catalyst is crucial, and its comprehension and fine tuning are still challenging. Many factors such as the morphology and the structure of the support and the ligation on the active site have important effects on the electronic structure of the active centers, which in turn strongly influence the catalytic properties [101].

The catalytic activity and selectivity of atomically dispersed metal catalysts can be tuned by modifying their ligands [100]. In particular it has been shown that organic ligands including heteroatoms such as P and N may have a remarkable impact on the electronic environments and hence on the corresponding catalytic performance [102]. Ligands also have important roles in stabilizing metals, to allow for stable organometallic aggregates and to avoid chemical or thermal degradation of the supported catalyst [103]. As a matter of fact considerable efforts have been put on rationalizing the effects of the ligand on the catalytic properties by systematic modifications of the latter [104–106]. Furthermore, metal-oxide supports and other molecules residing near the metal centers may also act as ligands and thus participate in tuning the catalytic properties [107–109]. As examples, Salas et al. have used the IL [Bmim][NTf<sub>2</sub>] in the catalytic hydrogenations of 1,3- cyclohexadiene (CYD), styrene (STY) and limonene (LIM) to show its effect on the efficiency of ruthenium nanoparticle (RuNP) catalysts. As a matter of fact, ILs are defined as salts with a melting point below the boiling point of water [44], and while they are used as conventional organic solvents, they also show a wide range of electron-donor/acceptor properties [110]. Bi et al. have conducted both experimental and computational studies for the mechanism of CO<sub>2</sub> reduction on Ru<sub>3</sub>CO<sub>12</sub> catalysts in the presence of ILs (BmmimCl, B<sub>3</sub>MimCl and BmimCl) in order to investigate the effects of imidazole chloride on the carbonylation of olefins with CO<sub>2</sub> [111]. They have reported that the imidazolium cation is activated by the chloride anion and forms the Ru-H active species with the catalyst precursor easily with a low energy barrier of 12.2 kcal mol<sup>-1</sup>. Consequently, CO<sub>2</sub> is inserted into the formed Ru–H bond with the assistance of the chloride anion to produce the Ru-COOH species which enables the activation of  $CO_2$ . They have concluded that the reduction of  $CO_2$  can be achieved easily in the order:  $BmmimCl < B_3MimCl \sim BmimCl.$ 

The possibility of controlling the electronic environment and the  $e^-$  donor/acceptor properties of atomically dispersed supported metal catalysts through ILs has been experimentally demonstrated. Babucci and co-workers have reported an experimental study in which they evaluated the effect of ILs on the electronic environment around the active sites in Ir(CO)<sub>2</sub> complexes bound to metal-oxide supports such as SiO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, and La<sub>2</sub>O<sub>3</sub> [112]. Even though the consequences of the ILs ligand effect on the reactivity and selectivity of an isolated metal center is known [112], to the best of our knowledge the mechanism of this effect has not been elucidated to date. Herein, we report the effects of ILs on the electronic environment of the active sites in a MgO supported-Ir(CO)<sub>2</sub> complex. To this aim we have performed DFT calculations to understand the mechanism of the IL's ligand effects on the catalytic properties of the atomically dispersed catalysts and suggest a representative model describing the interplay between the IL and the supported Ir(CO)<sub>2</sub> active center. Previous studies have shown that 1,3-dialkylimidazolium type ILs significantly affect the electronic properties of iridium carbonyls when they are chemically bound to supports [113]
Thus, we used two different ILs having different levels of electron donation tendencies on the supported Ir complexes: 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) and 1-butyl-3-methylimidazolium hexafluoro-phosphate ([Bmim][PF<sub>6</sub>]) interacting directly with Ir(CO)<sub>2</sub> complexes covalently tethered to a (MgO)<sub>n</sub> surface with different sizes (n = 2, 16, 20, 40, 80, Figure 5.1). Based on the experimental results [Bmim][OAc] represents the IL having a strong-electron-donating character on the Ir sites [72, 72, 114] whereas [BMIM][PF<sub>6</sub>] has an intermediate level-electron-donating capability. Although numerous recent studies investigating the structure and chemical performance of these types of metal-oxide supports are available in the literature [115, 116], those focusing on elucidating the interactions between ILs and metal- oxide supported catalysts, such as MgO–Ir(CO)<sub>2</sub>, are still rather scarce, and we plan to fill this gap with the present study.

## 5.2. Computational Methodology

DFT methods are known for being computationally efficient and most valuable to treat complex and large-size systems [46]. Furthermore, they represent the method of choice to correctly describe the electronic environment around the transition metals in the metal-oxide supports, also thanks to the possibility that they offer the opportunity of enlarging the size of the model [93]. In this study, we have used the PBE [87] functional to optimize the groundstate geometries of a metal-supported catalyst. The 6-31G(d,p) basis set has been used for C, H, O and Mg atoms while the LANL2DZ basis set developed by Hay and Wadt has been used for Ir, to allow the inclusion of a pseudopotential to partially treat the relativistic scalar effects [88]. Metal-oxide supports including transition metals are challenging systems for theoretical studies because they have partially filled d-orbital shells leading to a high density of states lying in a very narrow energy range, and eventually in multiconfigurational systems [117]. Yet, the PBE functional has been widely used for predicting structures and energetics of transition metal containing species [89]. Wang has reported the accuracy of the PBE functional for transition metals by performing calculations involving small scandium clusters (Sc<sub>n</sub>, n = 1-3), also validating our chosen approach [118]. In this study, all the computations have been carried out with the Gaussian 09 series of programs [49]. The electrostatic potential of the supported catalyst has been analyzed by computing the point

charges distribution with the CM5 and the Hirshfeld protocol [51]. As a matter of fact, the CM5 model is an extension of Hirshfeld population analysis and is also applicable to charged and uncharged molecules in a vacuum and in solution [119]. Electrostatic potential maps (EPM) have been generated as single points on top of the PBE optimized geometries using the M06-2X functional together with the 6-31G(d,p) bases for lighter atoms and LANL2DZ for Ir. The representative models taken into account in this study for the MgO supported-Ir(CO)<sub>2</sub> complexes with different faces ((100) and (110)) have been constructed by adopting the experimental data [100]. All the DFT calculations have been performed in the gas phase (298K and 1 atm).



Figure 5.1. Structures considered in this study: (A) metal-oxide supported Ir(CO)<sub>2</sub> complex, (B) [Bmim][OAc], and (C) [Bmim][PF<sub>6</sub>].

## 5.3. Results and Discussion

## 5.3.1. Ir(CO)<sub>2</sub>(MgO)<sub>n</sub> complexes

Early experimental and computational studies have reported that the accurate morphology of active metal centers and their mutual interactions with the support are fundamental to rationalize the influence exerted by the metal-oxide support on the chemical reactivity, including catalytic efficiency and selectivity [120]. Molecular modeling is therefore fundamental to provide an electronically-resolved picture of the catalyst in interaction with its environment [121]. In this study, we perform ab initio modeling of the complex system, especially considering the metal-oxide supports with or without the presence of an IL molecule near the metal center. To allow for a computationally less expensive approach we have resorted to the use of cluster models of the supported surface instead of periodic systems, as already reported in the literature [122]; this approach also has the advantage of allowing the more straightforward use of hybrid or meta-hybrid functionals and all the arsenal of molecular-based quantum chemistry methods. MgO can be used as a support for metal and bimetallic clusters for catalytic reactions. While periodic systems should be considered, the  $(MgO)_n$  clusters are reasonable models of the metal-oxide supported materials and can also be realized and actually used as nanosized catalytic reactors [95]. In addition, MgO is well-characterized experimentally and theoretically [95]. Hussein et al. have shown that MgO(100)-supported AuPd clusters generally form stable metal-oxide-supported complexes [123]. Furthermore, Han et al. also performed DFT calculations to study the migrations of a heavy Ir atom and Ir<sub>3</sub> clusters on MgO(100) and MgO(110) surfaces, respectively, calculating the migration barriers and binding energies of Ir to the different surfaces. They concluded that while an Ir atom is adsorbed on the MgO(100) surface, an Ir<sub>3</sub> cluster migrates on the MgO(110) surface [124]. Some of us have also previously reported in the case of the MgO(100) supported-Ir(CO)<sub>2</sub> complex, that Ir binds to the surface through two Ir–O bonds in agreement with the experimental findings (Figure 5.2) [81].

Different MgO crystals have been selected to model various  $(MgO)_n$  (100) supported Ir(CO)<sub>2</sub> complexes (n = 2, 16, 20, 40, 80) without including the IL. Besides the  $(MgO)_n(100)$  faces, we have also modeled a cluster of  $(MgO)_2$  metal-oxide supports presenting a (110) face. Hoffman et al. [95] reported that Ir atoms in the complexes bond with oxygen atoms of the MgO surfaces. These complexes can be bipodal having two Ir–O bonds, depending on the metal loading. In this study,  $(MgO)_n$  supported Ir(CO)<sub>2</sub> complexes were modeled as bipodal due to excellent agreement with experiments [81]. Hoffman et al. [95] used DFT calculations to provide further insight to the properties of the MgO surface species by using different charged Ir atoms such as Ir(I) and Ir(II). According to their results, the Ir–O bond distances increase with decreasing the Ir charge. Thus, they have reported that the bond dis-

tances and bonding sites also depend on the oxidation state of Ir atoms. Therefore, we have constructed our models by taking into account the Ir(0) and Ir(I) oxidation state to check the effect of the charge on the behavior of the active site in the complexes. Experimentally extended X-ray absorption fine structure (EXAFS) are considered to provide evidence for the interactions between Ir(CO)<sub>2</sub> and the supports [123]. Babucci et al. [112] have determined experimentally the EXAFS fit parameters for the MgO supported Ir(CO)<sub>2</sub> complex. In order to verify the bonding of  $Ir(CO)_2$  to these supports, we computed the bonding distances such as Ir-O<sub>support</sub>, Ir-C<sub>CO</sub>, Ir-O<sub>CO</sub> and Ir-Mg for each sample as shown in Table 5.3. Based on our calculations, the Ir-O<sub>sup</sub>, Ir-C<sub>CO</sub>, Ir-O<sub>CO</sub> and Ir-Mg bond distances are rather short: 2.23, 1.85, 3.03 and 3.01 Å, respectively for <sup>2</sup>[(MgO)<sub>2</sub>0Ir(0)(CO)<sub>2</sub>] (110) (3), hence justifying the formation of a stable complex. The obtained values are not extremely dependent on the topology of the support surface, indeed in the case of  $(MgO)_n(100)$ , these distances were determined in the range of 2.10-2.14 Å for Ir-O<sub>sup</sub>, 1.85 Å for Ir-C<sub>CO</sub>, 3.01-3.02 Å for Ir–O<sub>CO</sub> and 2.68–2.75 Å for Ir–Mg bonds. Although the variations in the distances are rather small, it appears that models with MgO(100) faces (1, 2, 4, 5 and 6) are in better agreement with the experimental EXAFS parameters especially concerning the Ir-Mg distance, which is the most affected (Table 5.3). We have also analyzed the electronic properties of the complexes such as the nuclear magnetic moment  $\mu_N$  (for Ir) and the band gap values ( $\Delta E$ ) for the different sized uncoated complexes (Table 5.2). As expected the nuclear magnetic moment ( $\mu_N = 0.159$ , Table 5.2) for the Ir atoms is almost identical in all the complexes. A greater variability may be found for the band gap values, which are usually smaller for Ir in the oxidation state 0 than for +1. In particular complex 6 reaches a gap close to 2.0 eV (Figure 5.2). This is probably due to a larger stabilization of the valence band indicative of a greater stabilization of the complex.

In addition to the equilibrium geometries, we have also considered the calculated vibrational frequencies. In particular we focused on the the  $v(CO)_{asym}$  and  $v(CO)_{sym}$  band positions and have compared them with the experimental data ( $v(CO)_{asym}$ : 1983,  $v(CO)_{sym}$ : 2068 cm<sup>-1</sup>) measured in the present study [100]. The IR carbonyl stretching of the Ir complexes have been calculated by using a scaling factor of 0.986 as defined for the PBE/6-31G(d,p) level of theory to partially account for anharmonicity (Table 5.1) [125]. For the (MgO)<sub>n</sub>(100) complexes (1,2, 4, 5, and 6), the  $v(CO)_{asym}$  and  $v(CO)_{sym}$  frequencies fall

in the 1981–1995 cm<sup>-1</sup> and 2034–2051 cm<sup>-1</sup> ranges, respectively, whereas for the (MgO)<sub>n</sub> (110) cluster (3) the same frequencies are found at 1929 cm<sup>-1</sup> ( $v(CO)_{asym}$ ) and 1967 cm<sup>-1</sup> ( $v(CO)_{sym}$ ). Once again, the (100) surface in the case of the (MgO)<sub>n</sub> better reproduces the experimental findings as seen in Table 5.1. For this reason, all subsequent calculations including ILs have been performed on top of the (MgO)<sub>n</sub>(100) structures.

$(MgO)_n$ -Ir(CO) <sub>2</sub> models	$v(CO)_{asym}$ (exp: 1983)	$v(CO)_{sym}$ (exp: 2068)
1	1983	2034
2	1981	2037
3	1929	1967
4	1995	2051
5	1994	2049
6	1987	2043

Table 5.1. Calculated (scaled) and experimental (exp) vibration frequencies for uncoated  $Ir(CO)_2/(MgO)_n$  complex models (cm<sup>-1</sup>, PBE/6-31G(d,p)).

Table 5.2. Band gap values ( $\Delta E$ ), nuclear magnetic moment ( $\mu_N$ ) and the oxidation states of Ir atoms in the Ir (CO)<sub>2</sub>/(MgO)<sub>n</sub> complexes are

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Complexes	Complex number/state of Ir	Electronic	properties
		$\Delta E(eV)$	$\mu_N$
$^{2}[(MgO)_{2}Ir(0)(CO)_{2}]$	1/0	0.53	0.159
$^{2}[(MgO)_{16}Ir(0)(CO)_{2}](100)$	2/0	0.27	0.159
$^{2}[(MgO)_{20}Ir(0)(CO)_{2}](110)$	3/0	0.62	0.159
$^{1}[(MgO)_{40}Ir(I)(CO)_{2}]^{+}(100)$	4/+1	1.76	0.159
$^{1}[(MgO)_{40}Ir(I)(CO)_{2}]^{+}(100)$	5/+1	1.92	0.159
$^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}(100)$	6/+1	1.98	0.159

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Complexes		Dista	nces	
	Ir-O <sub>sup</sub> (exp:2.06)	Ir-C <sub>CO</sub> (exp:2.02)	Ir-O <sub>CO</sub> (exp:2.95)	Ir-Mg(exp:2.76)
$^{2}[(MgO)_{2}Ir(0)(CO)_{2}]$	2.10	1.86	3.03	2.67
$^{2}[(MgO)_{16}Ir(0)(CO)_{2}](100)$	2.13	1.85	3.02	2.75
$^{2}[(MgO)_{20}Ir(0)(CO)_{2}](110)$	2.23	1.85	3.03	3.01
$^{1}[(MgO)_{40}Ir(I)(CO)_{2}]^{+}(100)$	2.14	1.85	3.02	2.68
$^{1}[(MgO)_{40}Ir(I)(CO)_{2}]^{+}(100)$	2.14	1.85	3.01	2.73
$^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}(100)$	2.14	1.85	3.02	2.72



Figure 5.2. Structures for the uncoated  $(MgO)_{80}$ -Ir(I)(CO)<sub>2</sub> complexes (PBE/6-31G(d,p), (Å)).

## 5.3.2. Conformational analysis of ILs

As also demonstrated in our previous study (Chapter 3) [126], the cation and the anion of the ILs are held together via hydrogen bonds and interionic interactions [126]. The charges on the heteroatoms have been calculated to help the prediction of the location of hydrogen bonds on the atoms of interest (Figure B.1 and Figure B.2). Based on the charge distribution calculations: (i) five (for [Bmim][OAc], named from 1-[Bmim][OAc] to 5-[Bmim][OAc]) and four (for [Bmim][PF<sub>6</sub>], named from 1-[Bmim][PF<sub>6</sub>] to 4-[Bmim][PF<sub>6</sub>]) conformers for the ILs have been located corresponding to local minima on the IL's potential energy surfaces and are displayed in Figure B.3 and Figure B.4; (ii) the most positively charged hydrogen atoms on the imidazolium rings are those located at C2 positions, i.e. on the carbon between the two N atoms of the ring. Indeed, the C2 hydrogens of the [Bmim]<sup>+</sup> cation in each IL have a large positive charge (0.178 for [Bmim][OAc] and 0.175 for [Bmim][PF<sub>6</sub>] with CM5) (Figure 5.1, Figure B.1 and Figure B.2). This leads to the stabilization of the IL's when the anionic counterparts ([OAc]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup>) are proximal to the C2 atoms of the cations as shown in Figure 5.3



Figure 5.3. Optimized structures for the global minima of the ILs (PBE/6-31G(d,p)).

## 5.3.3. IL-coated complexes

Babucci et al. have reported that the electronic environments of the active metal centers in SACs are influenced by both the point of zero charge of the metal-oxide support and the electron-donor/acceptor character of the IL sheaths coating them [112]. According to their experimental findings, the MgO support has a strong electron-donor property. The electron density on the Ir atom in the MgO supported-Ir(CO)<sub>2</sub> complex increases by coating the complexes with [Bmim][OAc]. The coating is also beneficial to the catalytic performance of the metal-oxide supported catalyst as shown for the 1,3-butadiene hydrogenation in which high selectivity for butenes was observed upon coating the supported iridium complexes with electron-donor ILs [114]. Even though several experimental studies have been carried out to rationalize the combined effects of the support and the IL on the electronic behavior of the active sites in similar complexes [72, 81, 112], only limited theoretical and computational studies are available. Here, we want to assess the effect of ILs on the MgO supported-Ir(CO)<sub>2</sub> complexes by suggesting plausible routes for the electron flow. We have considered the anion-catalyst, cation-anion-catalyst and cation-catalyst-anion complexes. Two different orientations for the  ${}^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}(100)$  complexes coated with [Bmim][OAc] have been modeled by showing that the stability, as identified by the relative Gibbs free energies, of the [Bmim][OAc]-coated MgO(100)-supported Ir(CO)<sub>2</sub> catalyst decreases when passing from the 8 (6.4 kcal mol<sup>-1</sup>) to the 7 (0.0 kcal mol<sup>-1</sup>) arrangement. The metal-oxide supported  $Ir(CO)_2$  complex is expected to interact with the IL via H bonds. In the case of 7-[Bmim][OAc]-coated- $^{1}$ [(MgO)<sub>80</sub>Ir(I)(CO)<sub>2</sub>]<sup>+</sup> and 8-[Bmim][OAc]-coated- $[(MgO)_{80}-Ir(I)(CO)_2]^+$  complexes  $Ir(CO)_2$  is indeed hydrogen bonded to the cationic part of the IL ([Bmim]<sup>+</sup>) (Figure B.5). The IL's anionic counterion instead interacts with the metal-oxide surface oxygen giving equilibrium distances in the range 2.11–2.19 Å. Note that the organometallic complex and IL interact through the precursor including Ir atom, two carbonyl groups which is bonded to the metal-oxide support by means of two oxygen atoms (bipodal) (Ir(CO)<sub>2</sub>), and the [OAc]<sup>-</sup> moiety of the [Bmim][OAc] (Figure B.5). We have also located five different models for the [Bmim][PF6]<sup>-</sup>coated MgO supported-Ir(CO)<sub>2</sub> complexes (Figure B.6). For these species, the relative energies ranking the following order: 9  $(49.3 \text{ kcal mol}^{-1}) > 10 (47.2 \text{ kcal mol}^{-1}) > 12 (7.5 \text{ kcal mol}^{-1}) > 13 (0.6 \text{ kcal mol}^{-1}) > 11$  $(0.0 \text{ kcal mol}^{-1})$ . Hence, this picture is like the previous one as also shown by the hydrogen bond distances between the carbonyl atom of the precursor and cationic hydrogens, which vary from 2.49 to 2.87 Å (Figure B.6 and Figure 5.1). In addition, two F atoms of the anionic moiety of the IL, i.e.  $[PF_6]^-$ , interact with two surface Mg atoms on the support with distances of 2.12 and 2.20 Å  $(11-[Bmim][PF_6]-^1[(MgO)_{80}Ir(I)(CO)_2]^+)$ . The models for the coated MgO–Ir(CO)<sub>2</sub> complexes being the closest to the global minima and having good agreement with experimental data are displayed in Figure 5.6. Intermolecular and intramolecular forces can play major roles in the interactions of the species with each other [127].

In the coated complexes, the hydrogen atoms of the IL cation interact with the oxygen atoms on the carbonyl oxygen of the precursor through H-bonding. In addition, O and F atoms in the anions of ILs ( $[OAc]^-$  and  $[PF_6]^-$ ) can interact with Mg atoms on the support and via H-bonding with the hydrogen atoms on the cation. The most positively charged hydrogen atom on the imidazolium ring of the cation may also be identified as the most acidic proton [128]; and it is responsible for strongly localized and directional hydrogen bonding between the cation and the anion of the IL. As seen in the Figure 5.6, both the H bond interactions between the anion and the most positive cationic H atom as well as the interionic interactions between the Mg atoms on the support and O and F atoms of the anions participate in the enhancement of the global stability of the structure.

### 5.3.4. IR spectra of the coated complexes

The IR carbonyl stretching frequencies of the iridium dicarbonyls can be considered as a marker of the electron-donor/acceptor properties of the complex and of the effects of the electronic environment [115]. We have calculated the v(C2H),  $v(CO)_{asym}$  and  $v(CO)_{sym}$ band positions for the coated complexes (Table 5.7). In the presence of [Bmim][OAc], the band positions for  $v(CO)_{asym}$ ,  $v(CO)_{sym}$  were experimentally determined to be 1949 and 2042 cm<sup>-1</sup>, respectively [100]. Our calculated vibrational frequencies are 1980 cm<sup>-1</sup>  $(v(CO)_{asym})$  and 2039 cm<sup>-1</sup>  $(v(CO)_{sym})$  for the [Bmim][OAc]-<sup>1</sup>[(MgO)<sub>80</sub>Ir(I)(CO)<sub>2</sub>]<sup>+</sup> (7) complex, while [Bmim][OAc] coated <sup>1</sup>[(MgO)<sub>80</sub>Ir(I)(CO)<sub>2</sub>]<sup>+</sup> (8) yields frequencies of and 1965  $(v(CO)_{asym})$  and 2025 cm<sup>-1</sup>  $(v(CO)_{sym})$ . The analysis of our computational results for the [Bmim][OAc]-coated supported Ir complexes has pointed out that the model having the highest consistency with the experimental data present three stabilizing interactions: (i)

the hydrogen atoms of the imidazolium ring of the cation form favorable hydrogen bond interactions with the O atoms of the anion at distances of 1.95 and 2.71 Å; (ii) these same oxygen atoms in the anion ([OAc]<sup>-</sup>) are engaged in interionic interactions with the Mg atoms on the metal-oxide surfaces at distances of 2.11 and 2.19 Å; (iii) the carbonyl oxygen of the Ir(CO) group is well positioned to develop stable interactions with the hydrogen atom of the CH\_3 moiety of the anion (3.11 Å). On the other hand, the  $\nu(C2H)$ ,  $\nu(CO)_{asym}$  and  $v(CO)_{sym}$  vibrational frequencies were measured experimentally as 3128 (v(C2H)), 1967  $(v(CO)_{asym})$ , and 2057  $(v(CO)_{sym})$  cm<sup>-1</sup> for the [Bmim][PF<sub>6</sub>]-coated supported Ir complex, ( [100], Table 5.7). To rationalize this behavior, we have modeled the  ${}^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}$ (100) complex with [Bmim][PF<sub>6</sub>] in different arrangements: anion-cation-catalyst (9 and 10), cation-anion-catalyst (12 and 13), and cation-catalyst-anion (11) as shown in the Figure B.6. The  $\nu(CO)_{asym}$  and  $\nu(CO)_{sym}$  band positions were detected experimentally for the [Bmim][PF<sub>6</sub>]-coated MgO(100) supported Ir(CO)<sub>2</sub> complex as 1949 and 2042 cm<sup>-1</sup>, respectively [100]. In the anion-catalyst arrangements, the computed vibrational frequencies have been found at 3139 cm<sup>-1</sup> (v(C2H)), 1973 cm<sup>-1</sup> ( $v(CO)_{asym}$ ) and 2038  $cm^{-1} (v(CO)_{sym})$  for 9, and 3136 (v(C2H)), 1973 ( $v(CO)_{asym}$ ) and 2035  $cm^{-1} (v(CO)_{sym})$ for 10. In the cation-anion-catalyst conformation, these same vibration peaks are at 3146 (v(C2H)), 1973  $(v(CO)_{asym})$  and 2034 cm<sup>-1</sup>  $(v(CO)_{sym})$  for 12 and 3164 (v(C2H)), 1987  $(v(CO)_{asym})$  and 2048 cm<sup>-1</sup>  $(v(CO)_{sym})$  for 13. In 11 (cation–catalyst–anion arrangement), the vibrational frequencies are found at 3172 (v(C2H))), 1945 ( $v(CO)_{asym}$ ) and 2027 cm<sup>-1</sup>  $(v(CO)_{sym})$ . Overall, the frequency of the C2H band changes only slightly with the specific arrangements and the calculated results indicate the presence of hydrogen bond interactions between the cation and the anion: between the most positively charged hydrogen atom on the imidazolium ring of the  $[Bmim]^+$  cation and the  $[PF_6^{-1}]$  anion in the presence of the MgO supported-Ir(CO)<sub>2</sub> complex. When we compare the calculated  $v(CO)_{asym}$  and  $v(CO)_{sym}$  vibrational frequencies with the experimental results, a good agreement is observed for 9, 10, 12 and 13. Indeed, models 11 and 13 correspond to the global minima, 13 reflects the experimental findings the best for  ${}^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}$  (100) and has the cation-anion-catalyst arrangement (Table 5.7 and Figure B.6).

## 5.3.5. Electron flow in the presence of ILs

Babucci et al. [112, 113] have claimed that ILs and supports act synergistically to control the electron density on the iridium centers in the metal-oxide supported Ir(CO)2 complexes. They have reported that v(CO) band positions shift to lower wavenumbers by the addition of an electron-donor IL [112]; an occurrence which has been attributed to the donation of electrons to the metal sites of the metal-oxide supported  $Ir(CO)_2$  complex. We have thus carried out the charge distribution analysis for the uncoated/coated 6, 7 and 13 complexes to obtain further insights into the charge exchange and the electron flow between the catalyst and its environment (Table 5.6, Figure 5.4). In the case of the [Bmim][OAc]-coated complex with the cation–anion– $(MgO)_{80}$ –Ir(CO)<sub>2</sub> arrangement, the electron densities of the 1st (O1) and 2nd (O2) oxygen atoms on the anion of the IL decrease, whereas the electron densities of the Mg and O atoms (Mg2, Mg5, O6) and C and O atoms of the MgO supported-Ir(CO)<sub>2</sub> complex (C5, O3, C6 and O4) increase (Figure 5.2 and Table 5.6). These results show that the metal site is not the only moiety affected by the presence of the IL coating, instead the carbon and oxygen atoms of the carbonyl groups of the Ir(CO)<sub>2</sub> are also affected and their electron density increases due to electron transfer from the oxygen of the IL anion to the Mg atoms, nearest to the  $Ir(CO)_2$  complex and on the carbonyl group in the  $Ir(CO)_2$  complex (Figure 5.5). This result confirms the effect of the electron donor (O) and acceptor  $(Ir(CO)_2)$ groups in modulating the electronic environment of the metal-oxide supported Ir(CO)<sub>2</sub> complexes. Based on the charge distribution calculations performed in this study, the charges on the iridium atoms in the uncoated/coated complexes are 0.375 (CM5), 0.100 (Hirshfeld) for the uncoated (6) complex, 0.371 (CM5), 0.096 (Hirshfeld) for 7 and 0.373 (CM5), 0.099 (Hirshfeld) for the coated complexes 7 and 13, respectively (Table 5.4). The difference in positive charges between the uncoated (6) and [Bmim][OAc]-coated (7) complexes is 0.04 indicating that the electron densities on Ir in complex 7 increases by 0.04. In the case of the  $[Bmim][PF_6]$ -coated MgO supported-Ir(CO)<sub>2</sub> complex (13), the positive charges on the Ir atom in 13 decrease by 0.02 (CM5) and 0.001 (Hirshfeld) pointing to a slight increase in the electron density on Ir. Overall, the positive charge on Ir decreases by 0.04 (CM5 and Hirshfeld) and by 0.02 (CM5) and 0.01 (Hirshfeld) by coating the complexes with [Bmim][OAc] and [Bmim][PF<sub>6</sub>], respectively, showing an increase in the electron density on Ir in the presence of ILs (Table 5.4), consistent with the experimental findings [112, 113].

Complex	CM5	Hirshfeld
$6^{-1}[(MgO)_{80}Ir(I)(CO)_2]^+$	0.375	0.100
$7^{-1}[(MgO)_{80}Ir(I)(CO)_2]^+ - [Bmim][OAc]$	0.371	0.096
$13-^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}-[Bmim][PF_{6}]$	0.373	0.099

Table 5.4. Charge distributions on Ir atoms uncoated and [Bmim][OAc] and [Bmim][PF<sub>6</sub>]-coated Ir(CO)<sub>2</sub>/(MgO)<sub>80</sub> complexes (PBE/6-31G(d,p)).



Figure 5.4. Optimized structure of [Bmim][OAc] coated <sup>1</sup>[(MgO)<sub>80</sub>Ir(I)(CO)<sub>2</sub>]<sup>+</sup> (7) complex and its labeled atoms (PBE/6-31G(d,p)).

Table 5.5. Charge distributions on labeled atoms (Figure 5.4) of naked [Bmim][OAc] IL (PBE/6-31G(d,p), pop=CM5).

Atoms	Uncoated-	Complex	coated-Co	omplex
	Hirshfeld	CM5	Hirshfeld	CM5
01	-0.366	-0.390	-0.230	-0.344
O2	-0.332	-0.403	-0.225	-0.342
C4	0.126	0.175	0.192	0.235
H1	0.0502	0.150	0.0675	0.152

Atoms	Uncoated-Complex		coated-C	omplex
	Hirshfeld	CM5	Hirshfeld	CM5
Ir	0.100	0.375	0.096	0.371
C5	0.121	0.0819	0.125	0.0871
03	-0.0962	-0.143	-0.096	-0.144
C6	0.122	0.0841	0.115	0.0762
O4	-0.0941	-0.141	-0.103	-0.150
05	-0.309	-0.616	-0.308	-0.598
Mg4	0.322	0.709	0.326	0.714
06	-0.302	-0.617	-0.303	-0.619
Mg5	0.316	0.711	0.326	0.709
Mg1	0.392	0.757	0.405	0.762
07	-0.396	-0.776	-0.395	-0.809
Mg2	0.395	0.764	0.353	0.725
O10	-0.462	-0.773	-0.462	-0.756
08	-0.397	-0.776	-0.390	-0.778
Mg3	0.396	0.774	0.371	0.774
09	-0.396	-0.779	-0.394	-0.780
Mg6	0.484	0.799	0.404	0.743

Table 5.6. Charge distributions on labeled atoms (Figure 5.4) of uncoated and [Bmim][OAc] coated MgO-supported Ir(CO)<sub>2</sub> complexes (PBE/6-31G(d,p), pop=CM5).

Table 5.7. Calculated relative Gibbs free energies ( $\Delta G_{rel}$ ), dipole moments ( $\mu$ ), experimental and calculated vibration frequencies for the uncoated and  $[BMIM][PF_6]$  and  $[BMIM][OAc]coated MgO supported Ir(CO)_2 complexes (kcal.mol<sup>-1</sup>, PBE/6-31G(d,p), cm<sup>-1</sup>).$ 

Complexes			Calculated				Experimenta	1
	$\Delta G_{rel}$	v(C2H)	$\nu(CO)_{asym}$	$\nu(CO)_{sym}$	ή	$\nu(C2H)$	$\nu(CO)_{asym}$	$\nu(CO)_{sym}$
$6^{-2}[(MgO)_{2}Ir(0)(CO)_{2}]$	I	I	1987	2043	I	I	1983	2068
7-[Bmim][OAc]- <sup>1</sup> [(MgO) <sub>80</sub> Ir(I)(CO) <sub>2</sub> ] <sup>+</sup>	0.0	2946	1980	2039	16.5	I	1949	2042
8-[Bmim][OAc]- <sup>1</sup> [(MgO) <sub>80</sub> Ir(I)(CO) <sub>2</sub> ] <sup>+</sup>	6.4	2944	1965	2025	16.2	<b>در</b>	٠,	"
9-[Bmim][PF <sub>6</sub> ]- <sup>1</sup> [(MgO) <sub>80</sub> Ir(I)(CO) <sub>2</sub> ] <sup>+</sup>	49.3	3139	1973	2038	18.7	3128	1967	2057
10-[Bmim][PF <sub>6</sub> ]- <sup>1</sup> [(MgO) <sub>80</sub> Ir(I)(CO) <sub>2</sub> ] <sup>+</sup>	47.2	3136	1973	2035	16.5	"	"	"
11-[Bmim][PF <sub>6</sub> ]- <sup>1</sup> [(MgO) <sub>80</sub> Ir(I)(CO) <sub>2</sub> ] <sup>+</sup>	0.0	3172	1945	2027	25.9	"	"	,
12-[Bmim][PF <sub>6</sub> ]- <sup>1</sup> [(MgO) <sub>80</sub> Ir(I)(CO) <sub>2</sub> ] <sup>+</sup>	7.5	3146	1973	2034	16.6	"	"	"
13-[Bmim][PF <sub>6</sub> ]- <sup>1</sup> [(MgO) <sub>80</sub> Ir(I)(CO) <sub>2</sub> ] <sup>+</sup>	0.6	3164	1987	2048	13.7	"	"	"

Finally, Volkan Findik has also calculated the electrostatic potential map (EPM) for each structure to visualize the effect of the IL on the electron densities of the Ir atoms in the supported complexes [100]. The electron-excess and deficient regions are represented in red and blue colors, respectively. In order to follow the electron flow, the naked metal-oxide supported Ir(CO)<sub>2</sub> is compared with the complexes with different ILs such as [Bmim]<sup>+</sup> [OAc]<sup>-</sup> and  $[Bmim]^+$   $[PF_6]^-$  [100]. The Ir atom in the naked structure is colored in white, in the middle of the extreme points. The EPM indicates that the presence of ILs increases the electron density on the Ir itself, and the electron density on the IL is reduced. Overall the electron density is transferred through the support to the Ir atom. While the oxygen atoms and the CH<sub>3</sub> moiety of the [OAc]<sup>-</sup> anion are red in [Bmim][OAc], the same groups seem to be less negative in the [Bmim][OAc]-coated  ${}^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}$  complex, demonstrating the flow of electrons from the IL towards the support and the catalyst. These changes show that the electrons of the anionic part of the ILs flow from the most negative atoms of the anions to the  ${}^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}$  complex. These differences indicate that the electron donor capacity of the [Bmim][OAc] group is higher than the [Bmim][PF<sub>6</sub>] group. The Ir atom in the naked structure appears white, which should be correlated to a negligible electron density depletion or accumulation. The presence of the IL increases the electron density on the iridium itself, while the electron density on the IL is reduced compared to the corresponding complexes. Globally, this means that the electron density is transferred through the support to the Ir atom, indicating the presence of an indirect ligand effect of the IL layer on the supported metal complexes (Figure 5.5).



Figure 5.5. Schematic representation of the electron flow from the IL to the MgO supported Ir(CO)<sub>2</sub> complex for the [Bmim][OAc]-coated  ${}^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}$  (7) complex (PBE/6-31G(d,p), pop = CM5).

Babucci et al. have reported a linear relation between the interionic interactions in the presence of IL and the degree of electron donation to the active site of the atomically dispersed catalyst [113]. In the presence of an IL which has an electron-donor property, the metal center becomes more electron rich, resulting in red-shifts in the v(CO) frequencies. In the case of naked IL ([Bmim][OAc]) the hydrogen bonding interaction between the anion ([OAc]<sup>-</sup>) and the most positively charge H atom on the imidazolium ring of the cation ([Bmim]<sup>+</sup>) has an equilibrium distance of 1.45 Å. The carbonyl frequencies for the uncoated MgO (100) supported Ir(CO)<sub>2</sub> (6 in Figure 5.2) have been calculated as 1987 cm<sup>-1</sup> for  $v(CO)_{asym}$  and 2043 cm<sup>-1</sup> for  $v(CO)_{sym}$  (Table 5.7). When complex 6 is coated with [Bmim][OAc] (7, Figure 5.6), the corresponding distance changes to 1.95 Å and the v(CO)band stretching frequencies shift to 1980 cm<sup>-1</sup> for  $v(CO)_{asym}$  and 2039 cm<sup>-1</sup> for  $v(CO)_{sym}$ . These results also confirm the experimentally detected red-shifts in the presence of an electron–donor IL [112, 126].



7-[Bmim][OAc]-<sup>1</sup>[(MgO)<sub>80</sub>lr(I)(CO)<sub>2</sub>]<sup>+</sup>



13-[Bmim][PF<sub>6</sub>]-<sup>1</sup>[(MgO)<sub>80</sub>lr(l)(CO)<sub>2</sub>]<sup>+</sup>

Figure 5.6. Structures for the ILs coated  $(MgO)_{80}$ -Ir(I)(CO)<sub>2</sub> complexes (PBE/6-31G(d,p),

Å).

## 5.4. Conclusion

Atomically dispersed supported Ir complexes have been modeled on different sized metal-oxide supports namely  $(MgO)_n$  (n = 2, 16, 40, 80) naked and coated with ILs such as  $([Bmim][OAc] \text{ and } [Bmim][PF_6])$  by DFT techniques. The  $v(CO)_{asym}$  and  $v(CO)_{sym}$  band stretchings have been compared with the experimental results and may be seen as markers of the electron density reorganization induced by the IL's coating. The role of the IL on the band position has been determined by rationalizing the charge distributions and the bond lengths of the uncoated/coated complexes. The analysis of the charge model and of the EPM clearly points to an active role of the IL in changing the electronic distribution, not only of the Ir center, but also of the carbonyl groups and of the precursor. This effect can clearly significantly alter the catalytic properties, confirming the non-innocent role of the environment in modulating the reactivity of this complex system.

In summary, while the balance between Coulombic forces and hydrogen bonds plays a crucial role in understanding the effect of IL on the catalytic system, the presence of IL can deeply modify the electronic properties of the same catalysts and should be properly considered in the experimental design or catalyst optimization.

# 6. LIGAND MODIFICATION AND PROTON MOBILITY REACTION MECHANISMS ON THE ZEOLITE-SUPPORTED Rh(CO)<sub>2</sub> COMPLEX

## 6.1. Introduction

One of the significant catalysts is the atomically dispersed single site catalyst (SAC) containing transition metal and is widely used in petroleum, hydrogenation of fats, organic compounds and many other industrial processes [129]. The metal may be expensive however the size of metal particle can be modified and dispersed on the metal oxide support [130]. The smaller the metal particles, the higher efficiency can be obtained in the catalytic reactions. In single site atomically dispersed catalysts (SACs), the active metal center activates the reactants and simplifies the chemical reactions [131]. To keep the advantages of heterogeneous catalysts and minimize their drawbacks, scientists have synthesized atomically dispersed catalysts containing mononuclear transition metals such as Pd, Pt, Au, Ir and Rh bonded to solid supports such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub> and Zeolite [99]. Another issue having importance for this type of catalyst is the kind of ligand [100, 132]. A ligand is anchored to the single atom site in the catalyst and has major effects on electronic properties and catalytic activities of the single site catalysts [81, 113]. Ligands can change the selectivities and the rates of the reactions by either adjusting the electron densities or setting steric hindrance on transition state species [133]. Thus, choosing an appropriate ligand has a crucial role for chemical reactions that occurs in the presence catalysts.

Yardimci et al. have performed the hydrogenation reactions of 1,3-butadiene over MgO and zeolite supported rhodium catalysts to understand the effects of the structure of supports and ligands on the selectivity of 1,3-BD hydrogenation [134]. They investigated the impacts of electron-donor properties of the supports and the ligands on Rh, including reactive hydrocarbons and CO. They also tested MgO-supported rhodium dimers, zeolite-supported rhodium complexes and zeolite-supported rhodium clusters, each in the absence of CO in the 1,3-BD hydrogenation. They reported that Rh catalysts are highly active in

different forms for hydrogenation reactions. They concluded that the carbonyl ligands in the form of Rh complex are easily replaced by 1,3-butadiene species to undergo hydrogenation.

Khivantsev et al. performed the catalytic conversion of ethene to butadiene or hydrogenation to ethane on HY zeolite-supported Rh complexes to explain the impacts of ligand substitution on the catalytic reaction. They showed that the conversion of HY zeolitesupported  $Rh(CO)_2$  complexes into  $Rh(CO)(C_2H_4)$  species provides the conversion of  $C_2H_4$ into C4 hydrocarbons such as butadiene which is the main product with 90% selectivity [133].

Uzun et al. conducted the experimental studies on the synthesis and characterization of a site- isolated iridium diethylene complex supported on zeolite-supported Rh/Ir complexes to evaluate the ligand effects in the single site catalysis on alkene hydrogenation. They reported that the carbonyl ligands on the Rh /Ir in the catalyst are useful but they make the complex unreactive towards hydrogenations of olefins [135].

According to the DFT studies reported by Vummaleti and co-workers, CO ligands have no impacts on C-C coupling step of ethylene dimerization. They performed their studies in the cases of  $Rh(C_2H_2)_2/zeo$ ,  $Rh(CO)(C_2H_4)/zeo$  and  $Rh(CO)_2/zeo$  complexes. They found that the loss of CO ligand from the catalyst system results in the formation of diethene on the Rh complex and increases the butene selectivity [93].

Gates and co-workers also performed experimental studies for ethene hydrogenation reaction in the case of zeolite supported Rh complexes to compare the catalytic activities and selectivities of Rh(CO)(C<sub>2</sub>H<sub>4</sub>) and Rh(CO)<sub>2</sub> complexes. They tested the ligand effects on the converison of ethene into ethane and also the dimerization of ethene to butene. They reported that the selectivity for ethene dimerization to butene is lower for Rh(CO)(C<sub>2</sub>H<sub>4</sub>) than for Rh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complex [136]. Overall, the ligand modifications play a key role on the selectivities for the hydrogenations processes of the unsaturated hydrocarbons and one has to understand the reaction mechanisms [72]. Zeolite-supported catalysts have been commonly used in chemical reactions such as hydrogenation, dehydrogenation, hydroalkylation and catalytic reforming [71,137]. Furthermore, zeolites are known as significant acidic catalysts [138]. They have Brønsted-Acidic sites such as  $\equiv$ Si-O(H)-Al $\equiv$  [139]. These sites increase the catalytic activities for the zeolites [140, 141]. Zeolites are formed from aluminosilicates containing oxygen-sharing silicate, [SiO<sub>4</sub>]<sup>4-</sup>, and aluminate, [AlO<sub>4</sub>]<sup>3-</sup>. The trivalent aluminum has a negative charge within the crystal structure. Counterions, such as H<sup>+</sup>, are adsorbed on oxygen sites proximate to the aluminum centers, balancing the charge (Figure 6.1) [142]. The resulting acid sites are widely accepted as the catalytic site for hydrocarbon cracking, alkylation, and isomerization reactions in zeolites [142].

Sierka et al. have conducted DFT calculations for proton mobility on H-CHA, H-FAU and H- MFI types of zeolites [139]. They calculated relative energies of the proton located on oxygen atoms for different proton positions in the zeolite supports. They concluded that the oxygen atoms, having protons, located between Al and Si atoms are more stable and have acidic properties, note also that these protons can jump easily from one oxygen to another (Figure 6.1) [139].



Figure 6.1. Brønsted acidic site of a zeolite support and the proton jumping.

Ryder et al. have performed DFT studies for proton migration and hydrogen exchange on zeolite-supported catalyst to clarify the reaction pathways for proton jump on the zeolite model. They reported that acidic proton is not fixed to a specific oxygen on the zeolite support, it migrates from one site to the other. In addition, they show that the flexibility of the O-Al-O angle plays a significant role in the proton-hopping reaction [142]. Although, there are several experimental and DFT studies for proton transfer reactions on zeolite support [135, 143–146], electronic and structural properties of zeolite for the reaction mechanism of proton transfer remain unclear. Herein, our aim is to model the proton transfer reaction mechanism on the zeolite supported Rh(I) complex in order to understand the reaction mechanism and the changes in the electronic properties on the catalyst during the reaction by using computational tools. DFT is widely applied in catalytic science and facilitates the understanding of catalysis at the molecular level [147]. Rapid developments of catalysts need a deeper insights on explaining the reaction mechanisms in the catalytic systems [148]. In this work, we have performed DFT calculations by considering zeolite-supported Rh(I) complexes. Firstly, we have demonstrated a ligand exchange mechanism between CO and acetylene groups to suggest a convenient reaction mechanism for the ligand modification in the presence of a zeolite-supported Rh catalyst. Finally, we show the contribution of DFT in identifying the protonation reaction mechanism for the zeolite-supported Rh(CO)<sub>2</sub> and Rh(CO)( $C_2H_2$ ) complexes (Figure 6.2).



Figure 6.2. Schematic representation of the zeolite-supported Rh(I) complexes considered in this study for the ligand modification and proton transfer reactions.

### 6.2. Computational Methodology

All calculations have been carried out with the Gaussian 09 program on a zeolite support [49]. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [87] has been used as functional to optimize geometries with the 6-31G(d,p) basis set for C, H, O, Al atoms as well as the Los Alamos National Laboratory (LANL2DZ) basis set developed by Hay and Wadt for Rh [88]. For all calculations, Rh bonded two oxygen atoms and Al atoms are free but the others in the support are frozen (Figure 6.2). CM5 has been performed for charge distribution calculations [91]. The IR carbonyl frequencies of the zeolite-supported Rh(I) complexes have been calculated by using a scaling factor of 0.986 [125]. We used the ideal gas approximation at T = 298 K and 1 atm for the gas phase calculations.

### 6.3. Results and Discussion

### 6.3.1. Zeolite-supported-Rh(CO)<sub>2</sub> complex

In the experimental part of this study, different types of the zeolite supports have been used to determine a suitable type of the zeolite support for the ligand exchange reactions. The vibrational frequencies for the (CO)<sub>asym</sub> and (CO)<sub>sym</sub> band positions have been measured for 4 different kinds of zeolites such as CBV780 (DAY), CBV400 (DAY), CP811C ( $\beta$ -zeolite) and CP814E ( $\beta$ -zeolite) (A.Uzun private communications 2022). In the modelling the dimerization of ethylene and its hydrogenation over a zeolite supported Rh(I)-carbonyl complex, Vummaleti and co-workers have used zeolite support (Faujasite (FAU)) with a highly cubic structure [93]. In this study, we have modeled the zeolite-supported Rh(CO)<sub>2</sub> complexes as initial structures (IS) in three different ways mimicking the study of Vummaleti and co-workers [93]. We performed this study by using a small cluster of the zeolite support to reduce the computational costs. The initial structure (IS) models considered in this study are shown in Figure 6.3.



Figure 6.3. Optimized structures for the zeolite-supported no protonated/protonated Rh(CO)<sub>2</sub> complexes (IS) (PBE/6-31G(d,p), LANL2DZ for Rh atom).

In the first initial structure (IS), there is no protonated site on the zeolite-supported Rh(CO)<sub>2</sub> complex. To justify our models, we have tabulated  $v(CO)_{asym}$  and  $v(CO)_{sym}$  vibration frequencies and have compared them with the experimental data (Table 6.1). The  $v(CO)_{asym}$  and  $v(CO)_{sym}$  vibrations have been calculated as 2004 and 2063 cm<sup>-1</sup> for IS (Figure 6.3a), respectively. In the case of IS-O-H (Figure 6.3b), there is a proton (H) on the one of the oxygen sites of the zeolite support. The band positions for this structure are 2033 for  $v(CO)_{asym}$  and 2088 cm<sup>-1</sup> for  $v(CO)_{sym}$ . The IS-Rh-H (Figure 6.3c) structure has a proton on the Rh side of the catalyst. The vibration frequencies have been calculated as 2094 cm<sup>-1</sup> for  $v(CO)_{asym}$  and 2117 cm<sup>-1</sup> for  $v(CO)_{sym}$ . These results show us that our calculations have good agreement with the experimental findings (CBV780) in the case of Rh protonated IS ([Rh(H)(CO)<sub>2</sub>/zeo]) complex (Figure 6.3). Therefore, we have performed the ligand modifications and proton mobility reactions with the protonated species IS-O-H ([Rh(CO)<sub>2</sub>/zeo], Figure 6.3b) and IS-Rh-H ([Rh(H)(CO)<sub>2</sub>/zeo], Figure 6.3c) by considering them as initial structures.

Table 6.1. Calculated (scaled with 0.986) and experimental (Unpublished study of Uzun et al.) vibrational frequencies (cm<sup>-1</sup>) for protonated/no-protonated zeolite supported Rh(CO)<sub>2</sub> complexes (PBE/6-31G(d,p)).

Zeolite-Supported Rh(CO) <sub>2</sub> complex	Calcu	lated		Experimenta	1
	$v(CO)_{asym}$	$v(CO)_{sym}$	Zeolites	$v(CO)_{asym}$	$v(CO)_{sym}$
IS	2004	2063	CBV780	2052.1	2117.7
IS-O-H	2033	2088	CBV400	2048.3	2114.1
IS-Rh-H	2094	2117	CP811C	2047.3	2113.8
-	-	-	CP814E	2048.3	2113.2

### 6.3.2. Proton mobility

Acidic protons in zeolites are known to migrate from one side to another in the catalytic system [142]. Two different mechanisms have been suggested to determine the reaction pathway for the acidic proton mobility on the zeolite-supported Rh(I) complexes. In the first mechanism (Mechanism-1, Figure 6.4), it has been assumed that the protonation occurs after

the acetylene group comes to the reaction media (1) and it binds to the complex (2). In the second mechanism (Mechanism-2, Figure 6.5), the protonation reactions happen before the acetylene group comes into the reaction media to start ligand exchange reactions.

In the first mechanism (Mechanism-1), the acidic proton migrates between two atoms with an activation barrier of 17.3 kcal.mol<sup>-1</sup> (TS2-3). In the case of second mechanism (Mechanism-2), this transfer takes places with a barrier of 22.3 kcal.mol<sup>-1</sup> (TS-H-transfer, Figure 6.6). The reaction barrier for the Mechanism-2 is slightly higher than the one for Mechanism-1. One of the reasons behind this result is that acidic proton makes a strong bond with an oxygen atom in the support, when the acetylene group is added to the reaction media, the bond distance between oxygen and H elongates, and the acidic proton can easily attack Rh. Thus the proton mobility reaction occurs easily in the case of Mechanism-1 (see ISO-H (0.98 Å) and 1 (0.99 Å) complexes in Figures 6.4 and 6.5).

According to the theoretical calculations conducted by Sauer et al., an activation energy for the proton migration reaction on the zeolite support has been reported as  $13 \pm 3$  kcal.mol<sup>-1</sup> [149, 150]. Besides, in the cases of other calculations of Sauer et al. in proton hopping reactions between two oxygen pairs around the Al tetrahedron on the faujasite model of zeolite support (Figure 6.1), the reaction barriers have been found in the range of 16.0-26.2 kcal.mol<sup>-1</sup> [142, 151]. Based on the results calculated in the present study, the reaction barrier of the proton migration in mechanism-1 has a reasonable agreement with the findings of Sauer and co-workers (Figure 6.6) [142, 150, 151]. Therefore, the protonation reaction in this type of zeolite complex can occur easily after the addition of acetylene group to the complex.



Figure 6.4. Mechanism-1: Addition of acetylene followed by proton transfer from metal oxide support to Rh (PBE/6-31G(d,p)).



Figure 6.5. Mechanism-2: Proton transfer from the oxygen of the metal oxide support to Rh (PBE/6-31G(d,p)).



Figure 6.6. Potential Energy Surface (PES) diagrams for the reaction mechanisms for the proton transfer from metal oxide support to the Rh atom (PBE/6-31G(d,p)).

### 6.3.3. Ligand modifications

In this part of the study, we have modeled the ligand exchange reaction mechanisms between carbonyl and acetylene groups in the presence of zeolite supported Rh(CO)<sub>2</sub> complex. For this purpose, we have suggested three different mechanisms (path-a, path-b and path-c) for the ligand modifications. The mechanisms for the ligand exchange starts from the IS-O-H (Figure 6.7). In complex IS-O-H, the di-carbonyl groups are coordinated as ligands on the Rh side of catalysts, and the complex has one proton on the oxygen atom of the support. The coordination of first acetylene group to the Rh center forms complex 1, which leads to addition of  $C_2H_2$  group to the Rh atom in the catalyst to yield 2. The mechanisms start being different (path-a, path-b and path-c) after the formation of 2 (Figure 6.4). Thus, the reaction mechanisms for the ligand exchanges are similar for the three mechanisms until the formation of the third (3a, 3b and 3c) complexes.

In path-a, the proton on the oxygen side of the zeolite support in complex 2 attacks Rh, forming complex 3a, and then the ligand exchange reactions take place. The first carbonyl group is removed from the complex 3a, leading to 4a. After the removal of the first carbonyl from the complex, the second acetylene group is added to the reaction media and is attached to the complex, forming 5a and 6a, respectively. Finally, the removal of the second carbonyl group from the zeolite-supported  $[Rh(I)(CO)(C_2H_2)_2]$  (6a) complex yields  $[Rh(I)(C_2H_2)_2]$  as a final state (FS-a). The optimized structures such as initial state (protonated zeolite-supported [Rh(I)(CO)<sub>2</sub>] complex), transition states, intermediates, and final state ( $[Rh(C_2H_2)_2]$ ) in path-a are shown in Figures 6.4 and 6.8. The removal of first carbonyl occurs with an activation barrier ( $\Delta G^{\ddagger}$ ) of TS3a-4a=11.1 kcal.mol<sup>-1</sup> (Figure 10). Arrival of the second acetylene to the complex and removal of the second carbonyl group from the complex takes place with barriers of 17.8 and 10.4 kcal.mol<sup>-1</sup>, respectively (Figure 10). Note that the energetic values for the TS5a-6a and TS6a-FS-a have been calculated as 30.9 and 35.2 kcal.mol<sup>-1</sup>, respectively (Figure 6.11), indicating that this type of ligand exchange reaction mechanism in the presence of Rh protonated catalyst is not viable at room temperature. In the case of path-b the ligand exchange reactions happen on the oxygen protonated zeolite supported Rh complexes. In the complex 2, the first carbonyl group leaves from the complex to form 3b (Figure 8). After this removal, the second acetylene is added to the reaction media and sticks to the complex, forming complexes 4b and 5b, respectively (Figure 8). The final state corresponding to the FS-b is formed after the second carbonyl group leaves from the complex. The reaction barriers for the arrival of two acetylene groups have been calculated as 3.7 kcal.mol<sup>-1</sup> for the first acetylene (TS1-2, Figures 8 and 10), 8.9  $kcal.mol^{-1}$  for the second acetylene (TS4b-5b, Figures 8 and 10). In addition, the barriers for the leaving of two carbonyl groups have been found as 9.7 kcal.mol<sup>-1</sup> for the first CO and 17.8 kcal.mol<sup>-1</sup> for the second CO group (Figures 8 and 10). These results show that the reaction step corresponding to the removal of second carbonyl group can be identified as rate determining step for path-b. The energetic values of each species in path-b are not higher than 25 kcal.mol<sup>-1</sup>, indicating that it is possible to have this type of ligand exchange reactions at room temperature.

In path-c, the ligand modification reaction mechanism has been modeled in the following order: the addition of two acetylene (3c and 4c in Figure 9) groups and removal of the two carbonyl groups (5b and FS-b, see in Figure 9) from the complexes. The steps corresponding to formations of 5b, TS5b-FS-b and FS-b are the same for both path-b and path-c mechanisms, so they have the same energies in the potential energy surface diagrams. The activation barriers ( $\Delta G^{\ddagger}$ ) for the arrival of two acetylene group to the complex have been calculated as 3.7 kcal.mol<sup>-1</sup> for TS1-2 and 4.0 kcal.mol<sup>-1</sup> for the TS3c-4c. For the removal of the CO groups these barriers have been found as 7 kcal.mol<sup>-1</sup> for TS4c-5b and 17.8 kcal.mol<sup>-1</sup> for the TS5b- FS-b (Figure 10). We conclude that in path-c the energetics for the ligand exchange mechanism have lower values than in the case of path-a and pathb. The addition of the first acetylene group to the Rh (CO)<sub>2</sub> complex has a barrier of 3.7  $kcal.mol^{-1}$  in the three mechanisms (Figure 6.11). In path-a, before the departure of the first carbonyl group from the complex, the protonation of Rh occurs. Based on the charge distribution calculations, the charge on the Rh atom has been found as 0.520 in the case of complex 2, whereas the charge on the Rh atom has been calculated as 0.609 for the complex 3a (Figure 6.4, Table 6.2), indicating that the positive charges on the Rh atom increase by protonation as expected and its reactivity decreases. Furthermore, early experimental studies for determining the effects of interionic interactions on the electronic structures of the metal sites in the solid catalysts show that increasing of electron densities on the active sites of the catalysts brings about a weaker C-O bond strength in the CO group [36]. In this study, the C-O bond length is 1.16 Å for complex 2, while after protonation in path-a, the C-O bond length has been found as 1.14 Å for complex 3a (Figure 6.4). These results confirm that when the positive charge increases, the C-O bond length decreases. The calculations regarding the activation barriers for the removal of the first CO groups from the complexes also confirm these results: path-a  $(11.1 \text{ kcal.mol}^{-1}) > \text{path-b} (9.7 \text{ kcal.mol}^{-1})$ . The protonation of the active side of the catalyst results in the difficulties in not only the removal of the first carbonyl group from the complex but also addition of the second acetylene into the complex. The order of barriers related to arrival of the first carbonyl group is consistent with the barriers of the addition of the second acetylene group to the complexes (17.8 kcal.mol<sup>-1</sup> for path-a and 8.9 kcal.mol<sup>-1</sup> for path-b) (Figure 6.11). These calculated results indicate that the addition of a proton to the Rh atom in the precursor causes steric hindrance and makes it difficult for the second acetylene to arrive. In addition, the calculated reaction energies (31.2 kcal.mol<sup>-1</sup> for path-a and 5.6 kcal.mol<sup>-1</sup> for path-b) also demonstrate that path-a is endergonic as compared to path-b and path-c (Figure 6.11). Therefore, ligand modification between CO and acetylene group in the case of path-a is not easy as compared to path-b due to steric hindrance and electronic properties of the active site in the catalysts. In path-c, the removal of first CO (with a barrier of 7 kcal.mol<sup>-1</sup>, Figure 6.11) and arrival of acetylene group (4 kcal.mol<sup>-1</sup>, Figure 6.11) to the complex is slightly easier than the other paths. Therefore, the ligand modification reactions between acetylene and CO groups on the oxygen-protonated-zeolite-supported Rh(I) complexes can easily take place via path-c.

Table 6.2. Charge distributions on Rh atom for the complexes in the protonation mechanism (mechanism-1) (PBE/6-31G(d,p), CM5).

Complex	Charges on Rh
IS-O-H	0.470
1	0.465
TS1-2	0.474
2	0.520
TS2-3	0.617
3a	0.609















Figure 6.10. Reaction mechanism (path-c) for ligand exchange on metal oxide supported Rh complex (PBE/6-31G(d,p)).


Figure 6.11. PES diagrams for ligand exchange reactions (path-a, path-b and path-c) (PBE/6-31G(d,p), kcal.mol<sup>-1</sup>).

#### 6.3.4. Electronic properties

To elucidate of the ligand effect on the electronic environment of the active site (Rh) of the catalyst, we have also reported  $v(CO)_{asym}/v(CO)_{sym}$  band positions for the complexes including di-carbonyl groups (Figures 6.4, 6.5 and 6.10) complexes (Table 6.3). In the case of oxygen-protonated-zeolite-supported Rh(CO)<sub>2</sub> complex (IS-O-H) the  $v(CO)_{asym}$  and  $v(CO)_{sym}$  vibration frequencies are calculated as 2033 and 2088 cm<sup>-1</sup>, respectively. After the replacement of CO groups on the precursor (Rh(CO)<sub>2</sub>) with the acetylene groups, these frequencies are observed at 2022 cm<sup>-1</sup> ( $v(CO)_{asym}$ ) and 2076 cm<sup>-1</sup> ( $v(CO)_{sym}$ ) for 4c complex.

Complex 4c contains both di-acetylene and di-carbonyl groups. The calculated v(CO) frequencies for complex 4c show us that having only di-carbonyl groups bonded to the Rh atom in the catalyst has higher band positions than the complex including two acetylene and two carbonyl groups. These red shifts in the (CO) band positions take place with the ligand modification between CO and acetylene groups around the active site, since the electron density is transferred from Rh atom to the CO group leading to weaker bond strength and a longer bond length (1.85 Å between Rh and CO group in IS-O-H and 1.93 Å in 4c complex, Figure 6.10). Thus, the changes in electronic properties of active side of the atomically dispersed catalyst have significant impacts on the ligand replacement reactions.

Complex	v(CO) <sub>asym</sub>	v(CO) <sub>sym</sub>	
IS-O-H	2033	2088	
1	2029	2085	
TS1-2	2017	2078	
2	2040	2085	
TS2-3	2073	2115	
3a	2087	2126	
TS-proton-transfer	2095	2132	
protonated-Rh-complex	2096	2122	
3c	2043	2093	
TS3c-4c	2021	2073	
4c	2022	2076	

Table 6.3. Calculated (scaled) band positions for carbonyl groups in the complexes (cm<sup>-1</sup>, PBE/6-31G(d,p)).

# 6.4. Conclusion

The ligand modification reactions and the acidic proton mobility property of the zeolite have been modeled to clarify the mechanisms for these reactions by using computational tools. According to the DFT results reported in this study, paths b and c are suited for the ligand exchange reactions on the zeolite supported atomically dispersed catalysts. Another important remark from the present study is that introduction of the acetylene group on the zeolites support facilitates the migration of the acidic proton of the zeolite support from one side to another location.

# 7. THEORETICAL INSIGHT INTO THE SELECTIVITY AND CATALYTIC ACTIVITY OF 1,3-BUTADIENE HYDROGENATION OVER γ-Al<sub>4</sub>O<sub>6</sub> SUPPORTED Ir(CO) COMPLEX

#### 7.1. Introduction

Selective hydrogenation reactions of dienes is a significant process in chemical industries [152–155]. Particularly, 1,3-butadiene (1,3-BD) is known as a probe molecule for polymer manufacturing and purifying the olefin feedstock [156, 157]. The selective hydrogenation of 1,3-butadiene to 1- or 2-butene is known to increase the purity of alkene species without reducing their overall concentrations [158]. Four primary products—1-butene, cis-2-butene, and trans-2-butene from partial hydrogenation and n-butane from complete hydrogenation—are produced from varying completion levels of the 1,3-BD hydrogenation reaction [153]. Among these hydrogenation products, 1-butene is the desired product and widely used in different industries such as polymer, pharmaceutical, petroleum, necessitating an understanding of the selectivity for such a product, so the selectivity for 1-butene is quite important for the partial hydrogenation reaction of 1,3-BD.

The catalyst plays a specific role in determining the stereoselectivity and the level of completion of the reaction [159]. For example, certain catalysts may prevent the complete hydrogenation of butenes to butane, thereby selecting butenes [114]. Additionally, there are catalysts which demonstrate selectivity for stereoisomers, though these have yet to be documented. Atomically dispersed metal oxide-supported metal catalysts are heterogeneous, with metal atoms dispersed on a crystalline support. These types of catalysts are valuable for the hydrogenation of 1,3-BD, since they provide high catalytic activity and selectivity toward 1-butene formation [112, 160]. The principal mechanism of alkadiene hydrogenation by heterogeneous catalysts was first proposed by Horiuti-Polanyi in 1934 and consists of three steps: i) alkene adsorption on the hydrogenated metal catalyst, ii) hydrogen addition to the  $\beta$ -carbon atom of the alkene, iii) reductive elimination of the free alkene [160]. The catalytic activity of a chemical reaction provides useful information on the rate and the rate

determining step of the reaction [161]. Metal sites in atomically dispersed catalysts often need stabilizing ligands, which may affect the catalytic performance [103]. Metal oxide supports can act as ligands to stabilize the metal center, thereby restoring and/or enhancing the catalytic activity [99]. The morphology of the support, including the electron donor-acceptor properties, impacts the reactivity of the metal center, the identity of reaction intermediates, and the kinetics of the catalytic reaction [72, 112]. Another issue having significant impact on the selectivity is the nature of the metal in the active site of the atomically dispersed catalyst [162]. Transition metals like Ni, Pt and Pd are widely reported as impressive metals in the catalysts for the hydrogenation of alkenes [163]. Even though, the traditionally supported monometallic Pd catalysts offer high conversion rates from acetylene and 1,3-BD to ethylene and 1-butene, respectively, they usually display low selectivity since they promote the overhydrogenation and the polymerization of acetylene to benzene [164, 165]. Several experimental studies revealed that the Ag alloyed Pd single-atom catalysts exhibit high acetylene conversion rate and high selectivity to ethylene [75, 165, 166]. Particularly, for the selective hydrogenation of dienes such as 1,3-BD into mono-olefins, Group VIII metals such as Pt and Pd are usually known as efficient catalysts. Therefore, less active transition metals such as Ag, Rh, Ir have recently become of interest to increase the catalytic selectivity [164, 165].

DFT calculations are critical components for explaining highly complex reaction networks since they provide important information regarding the reaction intermediates, mechanisms and rate-determining steps [167]. These calculations may aid in the development of novel catalytic materials in conjunction with experimental techniques such as IR, X-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge structure (XANES) spectroscopy [99, 168, 169]. Mattsson et al. have reported in their studies that Perdew-Burke-Ernzerhof (PBE ) functional has been widely used for predicting the energetics of transition metal-containing species [89]. PBE functional has been extremely influential for performing actual calculations and predicting the overall barrier for the hydrogenation reactions of CO and CO<sub>2</sub> over the Cu/ZnO catalyst [170]. Furthermore, Sun and Chen have performed DFT calculations with PBE functionals for iridium-catalyzed hydrogenations of alkenes to compare the Ir(I)/Ir(III) and Ir(III)/Ir(V) mechanisms in the case of an Ir/P1N-type catalyst [171]. We have also demonstrated in our previous works that for structures involving transition metals, PBE calculations agree with experimental findings [81]. Wang and co-workers have carried out a density functional theory (DFT) study for the selective hydrogenation of 1,3-butadiene over  $Pt_1/Cu(111)$  and  $Pt_{4-line}/Cu(111)$  catalysts to understand the efficiency and selectivity of 1,3-BD hydrogenation catalysis by controlling the activity of C-H and/or C-C bond cleavage [165]. They observed that upon using  $Pt_1/Cu(111)$  and  $Pt_{4-line}/Cu(111)$  as catalysts, the reaction kinetics followed similar trajectories while different products were thermodynamically favored. To be exact,  $Pt_1/Cu(111)$  demonstrated selectivity for 1-butene, while  $Pt_{4-line}/Cu(111)$  was not selective for partial hydrogenation, producing butane. Thus, it is important for a functional catalyst to not only have high stability and activity but to also selectively produce the product of interest [165].

Kattel et al. conducted theoretical studies of  $CO_2$  hydrogenation to CO, CH<sub>3</sub>OH, and CH<sub>4</sub> compounds on metal-oxide supported catalysts such as Ni/-Al<sub>2</sub>O<sub>3</sub>, Pt/TiO<sub>2</sub>, Ru/TiO<sub>2</sub>, Cu<sub>4</sub>/-Al<sub>2</sub>O<sub>3</sub> [172] to understand the complex reaction network by means of key descriptors such as binding energies of the intermediates, promoter effects, binding strength, morphologies, and the size of the catalyst. They showed that these parameters are useful for tuning selectivity and controlling catalytic activity. While the hydrogenation of CO<sub>2</sub> is generally difficult due to the substrate's thermochemical stability, Kattel et al. found that CO<sub>2</sub> can be activated and hydrogenated relatively in the presence of the metal-oxide supported catalysts [172].

Babucci et al. [112] have investigated the effects of the supports on catalytic activity and selectivity for partial hydrogenation of 1,3-BD by altering the environment around the active sites in  $Ir(CO)_2$  complexes bonded to metal-oxide supports such as SiO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO and La<sub>2</sub>O<sub>3</sub>. They reported that the metal-oxide support can act as a ligand that influences the electron density on the metal sites. In particular, the electron donor character of the supports, which tune the electronic environments of the active sites of the catalysts, make the hydrogenation of the 1,3-BD more selective for butene formation [112]. As the electrondonor abilities of the metal oxides increase, iridium sites of catalysts become more electron rich and consequently become more selective for the 1-butene formation [81, 102, 173]. Lam et al. have also conducted a study on the selective hydrogenation of CO<sub>2</sub> into methanol to analyze the effect of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and ZrO<sub>2</sub> supports on catalytic activity and reaction selectivity [173]. They also reported that in the presence of Al<sub>2</sub>O<sub>3</sub>, an intermediate electron donor, the rate of CH<sub>3</sub>OH formation is about three times greater than with SiO<sub>2</sub>, a weak electron donor. In our previous work [81], we have modeled complexes such as SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- and MgO-supported Ir(CO)<sub>2</sub> to elucidate their electronic properties and stabilities and have concluded that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported Ir(CO)<sub>2</sub> complex has intermediate electron donor character, which is the key to explaining the selectivity and catalytic activity of the catalytic agent.

Vummaleti et al. have modeled the hydrogenation and the dimerization of ethene on the zeolite supported Rh(I) complex, ([Rh(I)(CO)(C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup>), to show the effects of the metal oxide supported Rh(I) complex on both the transformation of ethene into butene and the selectivity of the complex mechanism [93]. They have attracted considerable attention for the hydrogenation of ethylene on the metal-oxide supported Rh complexes. However, the reaction mechanism for semi-hydrogenation of 1,3-BD on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported Ir complexes remain ambiguous. Although, several experimental and theoretical studies focused on this problem, the convenient mechanism for the partial hydrogenation of 1,3-BD remains still insufficient [72,132,174–176]. Herein, we have similarly performed PBE calculations based on the Horiuti-Polanyi mechanism [160] for the 1,3-butadiene hydrogenation in the case of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported [Ir(I)(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex (Figure 7.1) to explain the reasons of the selectivity of the hydrogenation of 1,3-BD toward 1-butene, understand the effects of the atomically dispersed catalysts on the selectivity of the reaction and suggest an appropriate reaction mechanism for the hydrogenation of the 1,3-BD over metal-oxide supported Ir complexes.



Figure 7.1. Reaction mechanisms considered for 1,3-butadiene hydrogenation.

Vigne et al. have investigated the origin of the high selectivity for the hydrogenation of 1,3-butadiene on the  $Pt_2Sn/Pt$  (111) surface alloy by performing DFT calculations [177]. In this study Vigne et al. showed that the selectivity of products is pathway dependent, with pathways leading to partial hydrogenation products (e.g., 1-butene, 2-butene) or other intermediate species (e.g., 1,3- and 1,4-metallacycles). They reported that the first hydrogenation step is preferred at a terminal carbon, and the further hydrogenation to 1-butene has by far the lowest barrier.

The energetic span model introduced by Kozuch and Shaik is known as a useful tool for DFT calculations dealing with the catalytic cycle [178]. It helps to make a bridge between experimental and theoretical calculations for kinetics [178]. Furthermore, it is easy to explain and examine the efficiency of the heterogeneous catalyst by means of this model [178]. In the catalytic cycle, a computational study is dealing with state energies, whereas experimental studies consider rate constants [179]. According to the transition state theory, these terms (state energy and rate constant) are the same. The efficiency of the catalytic cycle is measured by the turnover frequency (TOF) [179]. Babucci et al have reported in their experimental studies that the reaction rates can be reported in terms of TOF by assuming that all the active sites in the catalyst are accessible for the chemical reaction [72]. In the DFT calculations, one transition state and one intermediate are used in the TOF calculations. These terms are known as TOF-determining step (TDTS) and the TOF-determining intermediate (TDI). The energy difference between TDTS and TDI can be defined as the energetic span ( $\delta E$ ) of the cycle. When the TDTS appears after the TDI,  $\delta E$  is the energy difference between these two state; but in the opposite situation, we must also add the reaction energy ( $\Delta$ Gr) to this difference as defined as [179]

$$\delta E = \begin{cases} TDTS - TDI & \text{if TDTS appears after TDI} \\ TDTS - TDI + \Delta Gr & \text{if TDTS appears before TDI.} \end{cases}$$
(7.1)

In this model, there are no rate-determining steps, rather rate-determining states. The energetic span model was improved by using Gibbs energies instead of rate constants [178]. Kozuch has reported that working with the state energies corresponding to Gibbs energies is physically more correct than rate constants [180, 181]. Kozuch has also shown that the  $\delta E$ 

represents the rate of a reaction performed in the presence of a catalyst [178, 181]. Herein, we want to explain the 1-butene selectivity for the hydrogenation of 1,3-BD in the case of  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support in terms of energetic span model. In order to verify our models for partial hydrogenation reaction mechanisms for  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(I)(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex, we have compared the calculated results with the experimental findings for the 1,3-BD hydrogenation reactions in the case of uncoated complexes reported by Babucci et al. [72].

#### 7.2. Computational Methodology

As a DFT functional, the PBE [87] exchange-correlation functional has been used to optimize geometries with the 6-31G(d,p) basis set for C, H, O, Al atoms as well as the Los Alamos National Laboratory (LANL2DZ) basis set developed by Hay and Wadt for Ir [88]. None of the atoms of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support were frozen for the hydrogenation reaction pathways. Charge distribution calculations have been performed by using the Charge Model 5 (CM5) [91]. To verify the transition states, intrinsic reaction coordinate (IRC) calculations were performed along with the reaction paths in both directions to connect the transition states with the reactants and products. The IR carbonyl frequencies of the ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>)<sub>n</sub> (n = 2,6)-supported Ir(CO)<sub>2</sub> complexes have been calculated by using the scaling factor such as 0.986 [125]. All computations have been carried out with the Gaussian 09 program [49]. We used the ideal gas approximation at T = 333 K and 1 atm for the gas phase calculations.

#### 7.3. Results and Discussion

Babucci et al. [72] have prepared atomically dispersed supported iridium di-carbonyl complexes with partially dehydroxylated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in order to use this complex as the catalyst for the partial hydrogenations of 1,3-butadiene hydrogenations. Before starting to model the mechanisms, we have constructed  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex to understand the nature of this type of catalyst used in the hydrogenation reactions of the olefins. For this purpose, we used a small model for  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support in order to optimize the computational time (Figure 7.2). For the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex,  $v(CO)_{asym}$  and  $v(CO)_{sym}$  band positions were calculated as 2033 and 2082 cm<sup>-1</sup>, respectively. In the case of  $\gamma$ -Al<sub>12</sub>O<sub>18</sub>-supported Ir(CO)<sub>2</sub> complex, these band frequencies were found as 2029 cm<sup>-1</sup> ( $v(CO)_{asym}$ )

and 2086 cm<sup>-1</sup> ( $v(CO)_{svm}$ ) (Table 7.1). These results are in agreement with those of Babucci et al. who detected the  $v(CO)_{asym}/v(CO)_{sym}$  band positions for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported Ir(CO)<sub>2</sub> complex as 1994 for  $v(CO)_{asym}$  and 2074 cm<sup>-1</sup> for  $v(CO)_{sym}$ . We have also carried out charge distribution calculations for each complex to assess the effect of the size of  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support on the electronic environment of the Ir atom in the complexes (Table 7.2). Based on the calculated results, the charge on Ir is 0.401 for  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex (Figure 7.2a)., 0.404 for  $\gamma$ -Al<sub>12</sub>O<sub>18</sub> supported Ir(CO)<sub>2</sub> complex (Figure 7.2b). The Ir-O<sub>support</sub>, Ir-C<sub>CO</sub>, Ir-O<sub>CO</sub>, and C-O<sub>CO</sub> bond lengths are similar for both complexes: 2.12, 1.85, 3.01 and 1.16 Å, respectively for  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex and 2.19, 1.84, 3.00 and 1.16 Å, respectively, for  $\gamma$ -Al<sub>12</sub>O<sub>18</sub> supported Ir(CO)<sub>2</sub> complex (Table 7.3). In summary, the stretching vibration frequencies of carbonyl groups  $(v(CO)_{asym}/v(CO)_{sym})$ , the bond distances (for Ir and oxygen atoms in the support and for the atoms on the  $Ir(CO)_2$  complex) and the charges on the Ir atoms in the complexes are nearly the same in the two  $(\gamma - Al_2O_3)_n$ (n = 2,6)-supported Ir(CO)<sub>2</sub> complexes (Tables 7.2 and 7.3). Therefore, we expect the selectivities and reactivities of the 1,3-BD hydrogenation process to be accurately modeled by the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complexes (Figure 7.2a).



Figure 7.2. The optimized structures of  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> and  $\gamma$ -Al<sub>12</sub>O<sub>18</sub> supported Ir(CO)<sub>2</sub> complexes (PBE/6-31G(d,p)).

Table 7.1. Calculated (scaled) band positions for  $\gamma$ -(Al<sub>2</sub>O<sub>3</sub>)<sub>n</sub> (n=2,6) supported Ir(CO)<sub>2</sub> complexes (PBE/6-31G(d,p), cm<sup>-1</sup>).

Complex	v(CO) <sub>asym</sub>	v(CO) <sub>asym</sub>
$\gamma$ -Al <sub>4</sub> O <sub>6</sub> /Ir(CO) <sub>2</sub>	2033	2082
$\gamma$ -Al <sub>12</sub> O <sub>18</sub> /Ir(CO) <sub>2</sub>	2029	2086

Table 7.2. Charge distributions (CM5) on Ir atoms in  $\gamma$ -(Al<sub>2</sub>O<sub>3</sub>)<sub>n</sub> (n=2,6) supported Ir(CO)<sub>2</sub> complexes (PBE/6-31G(d,p)).

Complex	Charges on Ir atoms	
$\gamma$ -Al <sub>4</sub> O <sub>6</sub> /Ir(CO) <sub>2</sub>	0.401	
$\gamma$ -Al <sub>12</sub> O <sub>18</sub> /Ir(CO) <sub>2</sub>	0.404	

Table 7.3. Calculated distances (Å) for the  $\gamma$ -(Al<sub>2</sub>O<sub>3</sub>)<sub>n</sub> (n=2,6) supported Ir(CO)<sub>2</sub> complexes (PBE/6-31G(d,p)).

Complex	Ir-O <sub>sup</sub>	Ir-C <sub>CO</sub>	Ir-O <sub>CO</sub>	C-O <sub>CO</sub>
$\gamma$ -Al <sub>4</sub> O <sub>6</sub> /Ir(CO) <sub>2</sub>	2.12	1.85	3.01	1.16
$\gamma$ -Al <sub>12</sub> O <sub>18</sub> /Ir(CO) <sub>2</sub>	2.19	1.84	3.00	1.16

### 7.3.1. Formation of the Reactants

Atomically dispersed metal catalysts on the metal-oxide supports also provide an ideal strategy for the highest efficiency for modelling chemical reactions [182]. The metal sites in the atomically dispersed catalysts often need stabilizing ligands which affect the catalytic performance [114, 183, 184]. The catalytic behavior of the catalysts can be altered by an-choring a ligand to the surface of the metallic site [72, 185]. Gates and co-workers conducted experimental studies to explain the ligand effects on the selectivity and reactivity for the industrial reactions such as alkene polymerization and hydrogenation of ethene [14]. They

reported that the ligands including CO can be used to tune the properties of the supported catalysts in the chemical reactions, and markedly improve the selectivities of some catalysts. The CO ligand also stabilizes the supported metals in the form of mono-atomic species by limiting their reductions and aggregations into metal clusters [99]. In addition, Vummaleti et al. tested the ligand effects of Rh(CO)(C<sub>2</sub>H<sub>4</sub>) and Rh(CO)<sub>2</sub> complexes on the catalytic activity and selectivity of the reactions. They concluded that ethene dimerization is lower for Rh(CO)(C<sub>2</sub>H<sub>4</sub>) than for Rh(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> complex [93]. Based on these findings, for modelling the saturation reaction mechanism,  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir]<sup>+</sup> bounded to one carbonyl and a terminal olefin should be considered as an initial structure in order to be compare our findings with the previous metal support catalyst reaction studies. Therefore, first of all, we modeled the ligand exchange reaction mechanism between  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex and 1,3-BD to obtain the reactants (1a, 1c) for the partial hydrogenation of 1,3-BD over  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support [93, 99]. Since the mechanisms for the formations of the 1-butene and trans-2-butene are the same until the addition of second hydrogenation and 1a is used as a reactant in every case.

For modeling the ligand replacements to get the reactants (1a, 1b and 1c), we have suggested two different mechanisms for the formation of reactants (1a and 1c). The reactions for the replacement start with the initial structures including only 1,3-BD (trans position for 1a and cis position for 1c) and catalyst ( $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub>) and continue with the Cat2CO-BD(trans) and Cat2CO-BD(cis) complexes. For both Cat2CO-BD(trans) and Cat2CO-BD(cis) complexes. For both Cat2CO-BD(trans) and Cat2CO-BD(cis) complexes, 1,3-BD stays away from the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex. The coordinations of the BD into the complexes form Cat2CO+BD(trans) and Cat2CO+BD(cis) complexes and, leading to removal of one carbonyl group from the catalyst to yield 1a (CatCO+BD(trans), Figure 7.3) and 1c (CatCO+BD(cis), Figure 6) ( $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup>) complexes. The optimized structures and the reaction coordinates for the ligand modifications between CO and BD groups are shown in Figures 7.3-7.5.



Figure 7.3. Reaction mechanism of the formation of reactant (1a) from Cat2CO-BD in the partial hydrogenations of 1,3-BD over  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support (PBE/6-31G(d,p), LanL2DZ for Ir atom).

According to the calculated results performed in this part of the study, in the potential energy surface diagrams (PES), the arrival of BD to the complexes occurs with activation barriers of 2.1 and 1.9 kcal.mol<sup>-1</sup> for 1a and 1c, respectively, indicating that it is easy to stick BD to the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex in every position (Figures 7.4 and 7.5). Furthermore, the removal of one carbonyl group from the complex to obtain the reactants (1a and 1c) ( $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex) takes place with a barrier of 17.6 kcal.mol<sup>-1</sup> for 1a (Figure 7.4) and 19.7 kcal.mol<sup>-1</sup> for 1c (Figures 7.5), indicating that formations of the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complexes such as 1a and 1c from  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complex are applicable at room temperature, but the forming of 1a is easier than 1c because of having lower barrier corresponding the constitution of the reactant.



Figure 7.4. PES for the reaction mechanism of the formation of reactant (1a) for the 1-butene and trans-2-butene formations from the partial hydrogenations of 1,3-BD over  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support (PBE/6-31G(d,p), LanL2DZ for Ir atom, kcal.mol<sup>-1</sup>, 333K).



Figure 7.5. PES for the reaction mechanism of the formation of reactant (1c) for the cis-2-butene formation from the partial hydrogenations of 1,3-BD over  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support (PBE/6-31G(d,p), LanL2DZ for Ir atom, kcal.mol<sup>-1</sup>, 333K).



Figure 7.6. Reaction mechanism of the formation of reactant (1c) from IS in the partial hydrogenations of 1,3-BD over  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support (PBE/6-31G(d,p), LanL2DZ for Ir atom).

## 7.3.2. Reaction Pathways

<u>7.3.2.1.</u> Hydrogenation of 1,3-butadiene to 1-butene. We have modeled the hydrogenation reactions of 1,3-butadiene in the presence of the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex. The partial hydrogenation of butadiene to form 1-butene starts from complex 1a. In complex 1a, the coordination of H<sub>2</sub> to the Ir center forms complex 2a, which leads to the addition of H<sub>2</sub> to Ir. Complex 2a undergoes addition of H<sub>2</sub> where the H atoms stick to the Ir center, forming complex 3a. The first hydrogenation step takes place at the C1 position leading to 1-butene-3-yl-radical, yielding 4a. Finally, addition of the second H yields complex 5a, ([Ir(CO)(C<sub>4</sub>H<sub>8</sub>)]<sup>+</sup>, with 1-butene coordinated to the Ir center.

The optimized structures in the mechanism of 1-butene formation, such as the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> catalyst are complex 1a, transition states, intermediates (2a, 3a and 4a), product (5a, 1-butene). Based on the calculated results, along the reaction coordi-

nate, the attachments of the hydrogen atoms to the Ir center have a relatively high activation barrier  $\Delta G^{\ddagger}_{rel}$  (TS2a-3a = 25.4 kcal.mol<sup>-1</sup>) compared to TS3a-4a = 12.8 kcal.mol<sup>-1</sup>, TS4a-5a = 16.8 kcal.mol<sup>-1</sup> (Figure 7.13). Therefore, the TS2a-3a step is identified as TDTS state for this mechanism. Thus, for the 1-butene formation the energetic value for the TDTS is found as 25.4 kcal.mol<sup>-1</sup> (TDTS-1). Note that the energetic value for the TDI, labeled as TDI-1 in the PES diagrams for 1-butene is calculated as -11.5 kcal.mol<sup>-1</sup>. The TDI-1 appears before the TDTS-1, so the  $\delta E$  value is equal to the energy differences between these two states. Thus, the value of  $\delta E$  is found as 36.9 kcal.mol<sup>-1</sup> and the formation of 1-butene from the hydrogenation of 1,3-BD on the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex is exergonic (Figure 7.13). Note that the energy value of even the highest-energy transition state corresponds to 25.4 kcal.mol<sup>-1</sup>, indicating that 1-2 addition of hydrogen atoms for the hydrogenation of the 1,3-butadiene in the presence of  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex leads to the formation of 1-butene.

7.3.2.2. Hydrogenation of 1,3-butadiene to 2-butene. The addition of the hydrogen atoms to C1 and C4 positions (1-4 addition) in the butadiene molecule on the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported  $[Ir(CO)(C_4H_6)]^+$  complex will yield the formation of 2-butenes (cis and trans). The second hydrogenation step is the key step to determine the product types. The reaction mechanism for the formation of trans-2-butene follows the same steps as the ones for 1-butene formation until the second hydrogenation step (4a) (Figures 7.7 and 7.8). Thus, the TDI structure is the same for both formations of 1-butene and trans-2-butene (TDI-1= -11.5 kcal.mol<sup>-1</sup>, Figure 7.13). The addition of the second hydrogen at C4 position occurs with a barrier of  $\Delta G^{\ddagger}_{rel}$  (TS4b-5b = 26.5 kcal.mol<sup>-1</sup>) which is higher than TS2a-3a = 25.4 and TS3a-4a = 12.8 kcal.mol $^{-1}$ , Figure 7.13). Therefore, the energetic value for the TDTS-2 has been found as 26.5 kcal.mol<sup>-1</sup> for the formation of trans-2-butene (Figure 7.13). In order to model the formation of cis-2-butene (5c), we have considered the cis conformation of 1,3-BD as an initial structure (1c), which is 3.0 kcal.mol<sup>-1</sup> less stable than trans 1,3-BD (1a, 7.13) but is still present in the environment (1%). The suggested mechanism via 1c, 2c, TS2c-3c, 4c is like the one reported for 1-butene (5a). The barrier of the attachments of the hydrogen atoms to the Ir side of the catalyst has higher value than the other states ( $\Delta G_{rel}^{\ddagger}$  for TS2c-3c is 34.2 kcal.mol<sup>-1</sup>) (Figure 7.13). Thus, the rate determining states have been determined as 34.2 kcal.mol<sup>-1</sup> for TDTS-3 and -10.5 kcal mol<sup>-1</sup> for TDI-2. As observed in the mechanism of 1-butene formation, the TDI-1 and TDI-2 have appeared before the TDTS-2 and TDTS-3, indicating that the values of  $\delta E$  are equal to 38.0 kcal.mol<sup>-1</sup> and 45.1 kcal.mol<sup>-1</sup>. We have also calculated TOF for each product (5a, 5b and 5c) based on Equation (7.2) to determine the selectivity of the partial hydrogenation of 1,3-BD. The equation is expressed as

$$TOF = \frac{k_B T}{h} e^{-\delta E/RT}$$
(7.2)

where  $k_B$  is Boltzmann constant, T is Temperature and, R is gas constant. The TOF values have been found as  $4x10^{-12}$  for 1-butene formation,  $7x10^{-13}$  for trans-2-butene formation and  $1.8x10^{-17}$  s<sup>-1</sup> for cis-2-butene formation. These values show us that the rate of formation of 1-butene is higher than the others.

At this stage, we have compared the calculated results with the experimental findings reported in the study of Babucci et al., [72] who showed that in the uncoated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex, the selectivity to butenes ranges from 24% for 1-butene to 15 % for trans-2-butene and 13% for cis-2-butene [72]. From these experimental results, the yield of 1-butene is 1.6- and 1.8-times higher than the one for trans-2-butene and cis-2-butene, respectively; that of trans-2-butene is 1.2-times higher than cis-2-butene. These experimental findings mirror the trend in TOF values of the products obtained from DFT calculations, in which 1-butene was found to be the main product as compared to both trans-2-butene and cis-2-butene (Figure 7.13). Based on the calculated TOF results with PBE/6-31G(d,p), the amount of 1-butene is 7 times higher than trans-2-butene.



Figure 7.7. Reaction mechanism for 1-butene formation from the hydrogenation of 1,3-BD over the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup>

complex (1a) (PBE/6-31G(d,p), 333K).



Figure 7.8. Reaction mechanism for trans-2-butene formation from the hydrogenation of 1,3-BD over the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup>

complex (1a) (PBE/6-31G(d,p), 333K).



Figure 7.9. Reaction mechanism for cis-2-butene formation from the hydrogenation of 1,3-BD over the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex (1c) (PBE/6-31G(d,p), 333K).

## 7.3.3. Catalyst Regeneration

A catalyst is a substance that increases the rate of a chemical reaction, without itself being consumed during the reaction. It must be regenerated after a chemical reaction [52]. Therefore, regeneration options are also briefly discussed. In the case of 1-butene formation, catalyst regeneration reaction process starts with the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [(Ir(I)(C<sub>4</sub>H<sub>8</sub>)] complex (5a) complex (Figure 7.10). First, the second carbonyl group arrives at the complex to form complex 6a with a barrier of 5.8 kcal.mol<sup>-1</sup> (TS5a-6a, Figures 7.10 and 7.13). After the attachment of the second carbonyl group to the complex, 1-butene can be removed from the complex to stay free with the barrier of 2.8 kcal.mol<sup>-1</sup> (TS6a-7a, Figure 7.13). The same procedure has been repeated for 2-butenes. The barriers for the addition of the second carbonyl groups have been calculated as 4.9 kcal.mol $^{-1}$  (TS5b-6b, trans-2-butene, Figures 7.11 and 7.13), 22.2 kcal.mol<sup>-1</sup> (TS5c-6c, cis-2-butene, Figures 7.12 and 7.13) and the removal of 2-butenes from the complexes occurs with barriers of 20.9 kcal.mol<sup>-1</sup> for trans-2-butene (TS6b-7b, Figures 11 and 13) and 20.0 kcal.mol<sup>-1</sup> for cis-2-butene formations (TS6c-7c, Figures 7.12 and 7.13). The reaction barriers related to the departure of butenes from the catalyst show that 1-butene can easily be removed from the reaction media compared to 2butenes (Figure 7.13). Based on the calculated results for the regeneration of the catalyst, in complex 5a, the interactions between terminal carbons (C1 and C2) and Ir atom in the precursor are within distances of 2.13 and 2.17 Å (Figure 7.7), while in the complexes 5b and 5c, these interactions are between the secondary carbon and not only Ir side of the catalyst but also Al side of the metal oxide support with the distances that range from 2.16 to 2.31 Å (Figures 7.8 and 7.9). These results also verify that various interactions between the secondary carbon atoms and hydrogens of the organic species and the Ir, Al and O atoms in the catalyst make it difficult for the 2-butenes to separate from the catalyst. After the removal of the catalysts from the complexes, we also modeled final structures, labeled as 8a, 8b and 8c, including only  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported Ir(CO)<sub>2</sub> complexes and the products (1-butene and 2-butenes) for each mechanism and the calculated energies are 18.9 kcal.mol<sup>-1</sup> for 8a, -23.1 for 8b and -22.1 kcal.mol<sup>-1</sup> for 8c (Figure 7.13).

In summary, with the help of these suggested mechanisms, the selectivity of the partial hydrogenation of 1,3-BD over  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> support toward 1-butene can be explained easily.



Figure 7.10. Catalyst regeneration reaction mechanism for the 1-butene formation from over the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(I)(C<sub>4</sub>H<sub>8</sub>)] complex (5a) (PBE/6-31G(d,p), 333K).





complex (5b) (PBE/6-31G(d,p), 333K).



Figure 7.12. Catalyst regeneration reaction mechanism for the cis-2-butene formation from over the  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(I)(C<sub>4</sub>H<sub>8</sub>)] complex

(5c) (PBE/6-31G(d,p), 333K).



Figure 7.13. Potential Energy Surface (PES) diagram (kcal.mol<sup>-1</sup>) for the hydrogenation of  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [Ir(I)(CO)(C<sub>4</sub>H<sub>6</sub>)] to 1-butene, trans-2-butene and cis-2-butene (PBE/6-31G(d,p), kcal.mol<sup>-1</sup>, 333K).

#### 7.4. Conclusion

The hydrogenation mechanisms of 1,3-butadiene in the presence of atomically dispersed catalysts such as  $\gamma$ -Al<sub>4</sub>O<sub>6</sub> supported [(Ir(I)(CO)(C<sub>4</sub>H<sub>6</sub>)]<sup>+</sup> complex have been studied within the DFT framework to reveal the effect of possible reaction mechanisms on the rate and selectivity of the Ir-catalyzed reactions. Three reaction pathways modeled in this study deliver deeper insight into plausible mechanisms for this type of hydrogenation. The calculated results performed in the first part of this study show that the size of the model for the metal oxide support does not have a significant effect on the catalytic and electronic properties of the metal oxide supported catalyst (Tables 7.1-7.3). In the regeneration of catalyst reaction mechanisms, the height of the barriers related to removal of butenes from the catalyst depend on the interactions between double bond in the carbon chains and the catalyst. In the case of 1-butene formation, the double bond is located between terminal carbons (C1 and C2) and interacts with the Ir side of the catalyst with the distances of 2.49 and 2.77 Å, corresponding to an average distance 2.63 Å for this interaction (Figure 7.10). For 2-butenes, there is a bond between secondary carbons (C2 and C3) and interactions are with the Al side of the catalyst with distances of 2.16 and 2.62 Å: trans-2-butene, with 2.39 Å average distance (2.15 and 2.65 Å) and cis-2-butene, with 2.40 Å average distance Figures 7.11 and 7.12. Based on these calculated results, the interactions having importance for the removal of the product are weaker in the case of 1-butene formation than the others. Consequently, the lower distances between the double bond and the catalyst result in a higher barrier for the removal of the product.

According to energetic span model,  $\delta E$  values for each product have been calculated as 36.9 for 1-butene, 38.0 for trans-2-butene and 45.1 kcal.mol<sup>-1</sup> for cis 2-butene. In addition, the TOF calculations have been performed to determine the rate of the formation of the products. The TOF values have been found for 1-butene, trans-2-butene and cis-2-butene as  $4x10^{-12}$ ,  $7x10^{-13}$  and  $1.8x10^{-17}$  s<sup>-1</sup>, respectively. These results have also confirmed the fact that 1-butene selectivity is higher than the 2-butenes due to the lower  $\delta E$  and higher TOF values than the others. Therefore, for the formation of 1-butene, catalyst regeneration can easily take place only for the 1-butene formation reaction, with lower barriers compared to the 2-butenes formations (Figure 7.13).

The energetic values of the barriers for the reactant formation, hydrogenation path and the catalyst regeneration are not higher than 25.0 kcal.mol<sup>-1</sup> in the case of 1-butene formation (Figure 7.13). These results are also confirmed that the catalyst, the reactants and the structures in the hydrogenation reaction mechanisms considered in this study were well suited and modeled by using DFT calculations. However, the  $\delta E$  values, playing important role in explaining selectivity, have been calculated greater than 25.0 kcal.mol<sup>-1</sup> for each reaction mechanism with the PBE functional and 6-31G(d,p) basis set. As a future work, the dispersion effect will be taken into account for the weak bonds in the reaction mechanisms. The basis set will be resized to improve the energetic values and to take into account all interactions. In addition, different functionals (M06-2x and PBE0) and basis sets such as Def2-svp and Def2-tzvp can be used for the evaluation of the effects of the suggested mechanisms on the selectivity of the partial hydrogenation of 1,3-BD.

# 8. CONCLUSION REMARKS

In the first part of the dissertation, the effects of the ILs on the selectivity of the Diel-Alder reactions are investigated by using DFT in order to understand the reasons behind the endo selectivity in the presence of ILs. It has been observed that hydrogen bonding interactions with ILs play significant roles on the endo-selectivity of the Diels-Alder reactions.

In the second part of the thesis, the computational studies are carried out to elucidate the influence of the metal oxide supports such as SiO<sub>2</sub>-,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- and MgO-, on the atomically dispersed catalysts (SACs) and stabilities of the complexes including Ir(CO)<sub>2</sub> and Ir(C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>. The computational results related to vibrational frequencies, charge distributions and bond dissociation energies (BDE) show that because of having electron donor properties the MgO supported-Ir(CO)<sub>2</sub> and Ir(C<sub>2</sub>H<sub>2</sub>)<sub>2</sub> complexes provide higher stabilities and electron densities on the Ir site of the complexes compared to SiO<sub>2</sub>- and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- ones.

Different sized MgO supported-Ir(CO)<sub>2</sub> complexes are constructed to model ILs to explain the role of the ILs and find the reasons for the changes in the electronic properties dominating the catalytic properties of the atomically dispersed catalysts. In order to justify the models, the calculated  $v(CO)_{asym}$  and  $v(CO)_{sym}$  band positions are used to compare with the experimental data. In addition, charge distributions are used to explain the effects of the ILs on the electronic properties of the catalysts. Based on the calculated results reported in this thesis, ILs can easily interact with the catalytic system through hydrogen bonds and interionic interactions. It can be also noticed that in the presence of electron-donating ILs, the electron densities on the active sites of the catalysts increase via the electron flowing from the anionic part of the ILs to carbonyl groups of the precursor by means of the oxygen side of the metal oxide support. Accordingly, the electronic properties and catalytic activities of the SACs can be changed by tunning ILs.

Zeolite supports are widely used in the chemical reactions. Zeolites have also acidic properties. Catalytic and electronic properties of the atomically dispersed catalysts including zeolites can be changed by modifying different ligand around the catalyst. Since the proto-

nation site of the Rh causes the steric hindrance, the ligand replacement reactions should occur when the proton is located on the oxygen site of the metal oxide support in the zeolite.

1-butene selectivity is the main issue for the hydrogenation of the olefins in the case of heterogeneous catalysts having wide applications in the chemical industry. Although there are several experimental and computational studies conducted to understand the reasons behind the 1-butene selectivity, the reaction mechanism for the hydrogenation of the 1,3-BD is unclear. For this purpose, different reaction mechanisms for the hydrogenation of 1,3-BD and the regeneration of the catalyst are modeled in this thesis in order to understand the reasons behind the 1-butene selectivity by using the energetic span model.

Overall, thanks to DFT, reactions including SACs can be analyzed at the molecular level by modeling the structures and suggesting reaction mechanisms for the catalytic reactions. Comparison with the experimental values-wherever possible- can be used to confirm the methodology used and justify the suggested reaction mechanisms.

All in all DFT calculations are widely applied in catalytic science and predictions for future new experiments are expected to enrich the scientific community.

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# APPENDIX A: ROLE OF IONIC LIQUIDS ON THE SELECTIVITY AND THE RATE OF ORGANIC REACTIONS



Figure A.1. Structures of endo(n)/exo(x) products for the Diels-Alder reaction between CP and acrolein (1) in [Emim][N(Tf)<sub>2</sub>], their relative Gibbs free energies (B3LYP/6-31+G(d)) and dipole moments.



Figure A.2. Structures of endo(n)/exo(x) transition states for the Diels-Alder reaction between CP and acrolein (1) in [Emim][N(Tf)<sub>2</sub>], their relative Gibbs free energies (B3LYP/6-31+G(d)) and dipole moments.



Figure A.3. Structures of endo(n)/exo(x) products for the Diels-Alder reaction between CP and acrolein (1) in [Hbim][N(Tf)<sub>2</sub>], their relative Gibbs free energies (B3LYP/6-31+G(d)) and dipole moments.



Figure A.4. Structures of endo(n)/exo(x) transition states for the Diels-Alder reaction between CP and acrolein (1) in [Hbim][N(Tf)<sub>2</sub>], their relative Gibbs free energies (B3LYP/6-31+G(d)) and dipole moments.



Figure A.5. Structures of endo(n)/exo(x) products for the Diels-Alder reaction between CP and acrolein (1) in [Bmim][OTf], their relative Gibbs free energies given in parenthesis (B3LYP/6-31+G(d)) and dipole moments shown below for each species.



Figure A.6. Structures of endo(n)/exo(x) transition states for the Diels-Alder reaction between CP and acrolein (1) in [Bmim][OTf], their relative Gibbs free energies (B3LYP/6-31+G(d)) and dipole moments.



Figure A.7. Structures of endo(n)/exo(x) products for the Diels-Alder reaction between CP and methyl acrylate (2) in [Emim][N(Tf)<sub>2</sub>], their relative Gibbs free energies (B3LYP/6-31+G(d)) and dipole moments.



Figure A.8. Structures of endo(n)/exo(x) transition states for the Diels-Alder reaction between CP and methyl acrylate (2) in [Emim][N(Tf)<sub>2</sub>], their relative Gibbs free energies (B3LYP/6-31+G(d)) and dipole moments).



Figure A.9. CP and acrylonitrile (3) in [Emim][N(Tf)<sub>2</sub>], its relative Gibbs free energy given in parenthesis (B3LYP/6-31+G(d)) and dipole moments).



Figure A.10. Structures of endo(n)/exo(x) products for the Diels-Alder reaction between CP and acrylonitrile (3) in [Hbim][N(Tf)<sub>2</sub>], their relative Gibbs free energies (B3LYP/6-31+G(d)) and dipole moment).

# APPENDIX B: INFLUENCE OF IONIC LIQUIDS ON THE ELECTRONIC ENVIRONMENT OF ATOMICALLY DISPERSED Ir ON (MgO)(100)



Figure B.1. Charge distributions on cation and anion of IL ([Bmim][OAc]) (CM5 methods, PBE/6-31G(d,p)) (Red: negative , Blue: positive, Pink: carbon number).



Figure B.2. Charge distributions on cation and anion of IL ([Bmim][PF<sub>6</sub>]) (CM5 methods, PBE/6-31G(d,p)) (Red: negative , Blue: positive, Pink: carbon number).



Figure B.3. Conformers of [Bmim][OAc] and their relative energies (red) shown below for each species (PBE/6-31G\*\*, kcal.mol<sup>-1</sup>).



Figure B.4. Conformers of [Bmim][PF6] and their relative energies (red) shown below for each species (PBE/6-31G\*\*, kcal.mol<sup>-1</sup>).



Figure B.5. Structure of [Bmim][OAc] coated  ${}^{1}[(MgO)_{80}Ir(I)(CO)_{2}]^{+}$  complex.



Figure B.6. Structure of  $[Bmim][PF_6]$  coated  ${}^1[(MgO)_{80}Ir(I)(CO)_2]^+$  complex.

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