

**Suzuki Reactions Over
Palladium Loaded Y Zeolite**

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**A Dissertation Submitted to the
Graduate School in Partial Fulfillment of the
Requirements for the Degree of**

MASTER OF SCIENCE

Department: Chemistry

**Izmir Institute of Technology
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ACKNOWLEDGEMENTS

I would like to express my gratitude to Prof. Dr. Levent Artok, and Assist. Prof. Dr. Selahattin Yilmaz for their valuable supervision, encouragement and guidance during all phases of this study.

I would like to thank to Assoc.Prof.Dr. E. Ahmet Eroglu, Mr. Sinan Yilmaz and Ms. Asli Erdem for their warm and sincere efforts in helping the performing AAS analysis.

Financial support by the Research Funding Office of Izmir Institute of Technology is highly appreciated.

Finally, I want to thank my husband for his patience and understanding.

ABSTRACT

In this study, the use of Pd(II) loaded NaY type zeolite as a catalyst in the Suzuki carbon-carbon bond coupling reactions of aryl halides with aryl boronic acids was investigated.

For this aim, $\text{Pd}(\text{OAc})_2$, and $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ complexes were loaded into NaY zeolite in order to form an appropriate catalyst system. $\text{Pd}(\text{NH}_3)_4^{2+}$ loaded Y type zeolite was calcined to obtain Pd(II) form.

$\text{Pd}(\text{OAc})_2$ loaded Y type zeolite showed high activity in the reactions of 4-iodoanisole and 4-bromoanisole with arylboronic acid. However the reusability which is an important property of heterogeneous catalyst could not be provided, the following studies were continued with Pd(II) loaded Y type zeolite.

When, 4-iodo and 4-bromoanisole reactives were used in the presence of Pd(II) loaded Y type zeolite, 60-100% biaryl products were obtained. The amount and type of the base and DMF:H₂O ratio have high effects on the yield. In order to prove that the reaction took place in heterogeneous phase, at the end of the reaction Pd analysis of the solution was performed by AAS technique. It was found that the Pd amount in solution was trace.

ÖZ

Bu çalışmada, aril halojenürlerin aril boronik asit ile Suzuki karbon-karbon kenetlenme tepkimelerinde Pd(II) yüklü NaY tipi zeolitin katalizör olarak kullanılabılırılığı incelenmiştir.

Bu amaçla $\text{Pd}(\text{OAc})_2$, $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ kompleksleri Y tipi zeolite yüklenerek uygun katalizör sistemleri oluşturulmuştur. Paladyumun Pd(II) formunu oluşturmak amacıyla, $\text{Pd}(\text{NH}_3)_4^{2+}$ yüklü Y tipi zeolit kalsine edilmistir.

$\text{Pd}(\text{OAc})_2$ yüklü NaY 4-iyodoanisol ve 4-bromoanisol bilesiklerinin aril boronik asit ile tepkimelerinde yüksek aktivite göstermiş ancak heterojen katalizörün önemli bir özelliği olan tekrar kullanılabılırılık özelliği $\text{Pd}(\text{OAc})_2$ yüklü Y tipi zeolit için sağlanmadığından çalışmalara Pd(II) yüklü Y tipi zeolit ile devam edilmistir.

Pd(II) yüklü NaY tipi zeolit üzerinde 4-iyodo ve 4-bromoanisol reaktifler ile % 60-100 arasında bıarıl ürünleri elde edilmistir. Tepkime verimliliğinde kullanılan baz tipi ve miktarı, DMF:Su oranı önemli ölçüde etkili olmustur. Tepkimenin heterojen fazda gerçeklestigini gösterebilmek amacıyla reaksiyon sonunda çözeltide paladyum analizi yapılmış ve AAS analizi sonucu paladyumun çözeltide iz miktarda kaldığı saptanmıştır.

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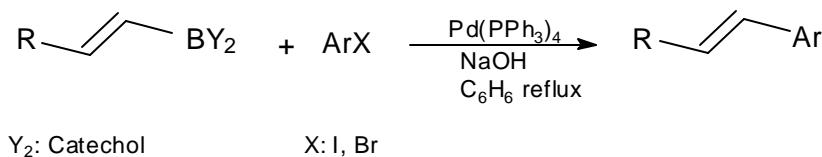
CHAPTER 1

INTRODUCTION

C-C bond formation reactions have been the most important reaction types for the synthesis of new organic materials, synthetic methodology for regio and stereo selective bond formation between unsaturated carbon atoms. They are also important structural units in drugs as well as in non-linear optical materials [1].

A number of new methods for the preparation of synthesis of organic reagents, which include C-C bond formation have been recently developed utilizing organometallic compounds; magnesium [2], aluminium [3], boron [4], silicon [5], copper [6], silver [7] reagents. After the discovery of palladium catalyzed reaction of Grignard reagents [8], many other organometallic reagents have proven to be highly useful as nucleophiles for the C-C bond formation reaction, e.g, organolithiums by Murahashi [9], organostannans by Migita [10] and Stille [11] and 1-alkenylcopper(I) by Normant [12], organosilicon compounds by Hiyama [13].

Fortunately, in 1981, Suzuki found that organoboron compounds, even organoboronic acids and esters, have sufficiently enough reactivity for the transmetalation to the other metals and he discovered the first palladium catalyzed cross coupling reaction between organoboron compounds and organic halides for the formation of carbon-carbon bonds (Scheme 1.1) [14]. Therefore this reaction has been called the Suzuki coupling, Suzuki reaction or Suzuki-Miyaura.



Scheme 1.1. The First Suzuki Coupling Reactions

The Suzuki coupling reaction offers several additional advantages, such as; the reactions are largely unaffected by the presence of water, very rapid, tolerate a broad

range of functional groups, usually complete within a few minutes of temperatures below 25 °C [15]. Moreover, the inorganic by product of the reaction is non-toxic and easily removed from the reaction mixture thereby making the Suzuki coupling is suitable not only for laboratories but also for industrial processes.

The advantages of organoboron compounds allow the increase of usage of this reaction in many areas. After discovery of Suzuki reaction, various modifications have been made for the reaction conditions. In this reactions various palladium complexes, bases and solvents were used. Such as; a combination of $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ and aqueous Na_2CO_3 in dimethoxyethane works satisfactorily in most cases [16,17]. The combination with other bases such as Et_3N [18], $NaHCO_3$ [16], Cs_2CO_3 [19], Tl_2CO_3 [20] and K_3PO_4 [21] with or without Bu_4NCl [22] have also been used. In addition to these studies; $Pd(OAc)_2$ with PPh_3 was used for self-coupling reaction of arylboronic acids under anhydrous conditions [23]. Wong reported self-coupling of organoboroxines catalyzed by $Pd(PPh_3)_4$ in a methanol/toluene solvent system [24]. Then he found that phosphine and phosphite are efficient ligands for palladium catalysed homo coupling of arylboronic acids in DMF [25]. Kabalka and co-worker [26] reported a ligandless palladium chloride catalyzed homo coupling of arylboronic acids in water or a water/ethanol mixture at room temperature. Excellent yields of the desired biaryl products were obtained. $PdCl_2(SEt_2)_2$ catalyst was used by Zim in the C-C bond formation reaction of 4-bromotoluene with phenylboronic acid at 130 °C [27].

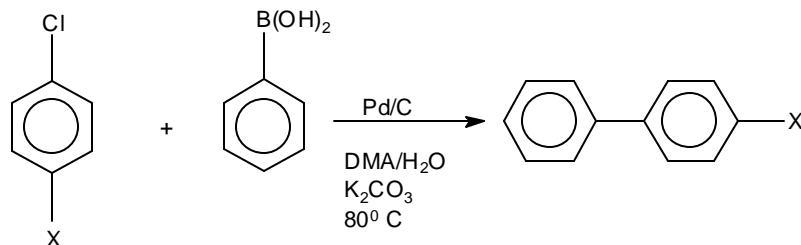
As seen in these studies, all reactions were carried out in homogeneous conditions. But there are a lot of disadvantages of using homogeneous catalysts. Recovery of expensive homogeneous complexes and their re-use may enhance economy of processes. At the same time, the catalyst recovery decreases pollution of desired products with hazardous or unhealthy compounds. Other promising expectations are the possible use of less expensive and environmentally friendly solvents and a better handling of the sensitive catalytically active complexes. For these reasons heterogenization of homogeneous catalysts is of growing interest in chemistry. When these problems are considered, heterogeneous catalysts are more preferable in C-C bond formation reactions.

Although the industrial use of heterogeneous catalysts is more desirable owing to the ease of catalyst separation and recycling, there are only very few reports of heterogeneous-reusable catalysts for the Suzuki reaction.

Pd/C is one of the most common heterogeneous palladium catalysts, and several studies demonstrated the application of Pd/C for the Suzuki-Miyaura coupling reaction. Tsukuda and his co-workers reported that Pd/C as a reusable catalyst for the coupling reaction of halophenols and arylboronic acids in aqueous media [28]. Before this study, there hadn't had any example for the Suzuki-Miyaura coupling of iodophenols in aqueous media.

Le Blond et al. [29] found that Pd/C, without added ligands, catalyses the Suzuki coupling reactions of aryl chlorides arylboronic acids.

The reaction, (Scheme 1.2.) proceeded smoothly with electron deficient aryl chlorides, gave moderate yields with neutral aryl chlorides but little conversion with electron rich aryl chlorides. Although re-usability is an important factor for heterogeneous systems, this property was not investigated in this study.



Scheme 1.2. Pd/C Catalysed Suzuki couplings with aryl chlorides

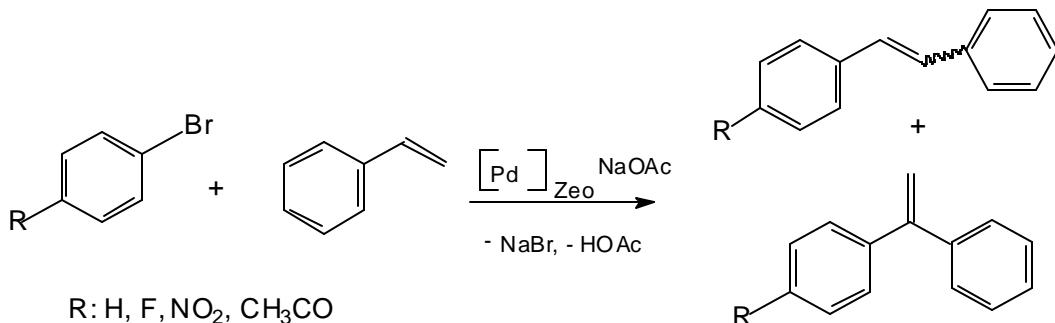
The second type of heterogeneous catalyst is polymer bound palladium catalyst. The polymer bound palladium catalysed cross coupling reaction of electrophiles (halides and triflates) with organoboron compounds to form carbon-carbon bonds has been achieved at mild conditions with very high activity. The polymeric catalyst can easily be separated from a reaction mixture and reused more than ten times with no decrease in activity [30].

The other important heterogeneous catalyst system is KF/?-alumina mixture. Kabalka and co workers [31] used this commercially available KF/?-alumina mixture, doped with a ligandless Pd(0) catalyst to develop a novel, solventless Suzuki cross coupling methodology. They found that both K_3PO_4 and KF were effective bases for solid-phase coupling reactions at 100 °C.

Varma and Naicker [32] reported the synthesis of biaryl compounds using a new system, $PdCl_2$ and tetraphenylphosphonium bromide-intercalated clay. These modified clay materials, unlike other conventional catalysts, enjoy considerable advantages such as ease of handling, recyclability and low cost.

Zeolites, which are environmentally benign have specific properties (ion exchange capability, crystalline structure with regular pores of molecular size) were utilized to prepare heterogeneous systems containing highly dispersed metals. For this instance, Kosslick et al. [33] used a palladium-phosphine complex loaded MCM-41 zeolite as a heterogeneous catalyst for the Suzuki reaction of 4-iodoanisole. They showed that the immobilization of palladium-phosphine complex on MCM-41 is a possible route to heterogenise the homogeneously catalysed Suzuki reaction. The activity of this catalyst was investigated over the cross coupling of 4-iodoanisole with phenylboronic acid. Results indicate that catalysts can be recycled and reused. The recycled catalysts show an enhanced activity but the leaching of the catalyst cannot be prohibited. The tedious silanization procedure requiring anchoring of a thiol siloxane and subsequent oxidation and the need of phase transfer surfactant are among the drawbacks for this Pd complex MCM-41 as compared to the Pd(II)-NaY zeolite reported here.

Heck reaction is one of the most important C-C bond formation reactions and occurs between aryl halides and olefins (Scheme 1.3.). In Heck reaction of bromobenzene with different substitution groups and styrene, Y-zeolite loaded with different palladium complexes have been used as heterogeneous catalysts by Djakovitch et al. [34-35].



Scheme 1.3. Heck Reactions Over Palladium Loaded Zeolite

Zeolites as supported systems can be used as heterogeneous catalysts. When zeolite is used as a heterogeneous catalyst, it provides several advantages to the reaction. Immobilization of palladium complexes in the zeolite supercages is one advantage of zeolites. The immobilized palladium complexes have the same activity as their free form in solution. Microstructure of zeolite could also help to overcome the problems of leaching in solution. In addition, zeolites are capable of stabilizing intermediate active species retained in their cavities due to their shape selectivity.

In a work simultaneously done with our work, bifunctional zeolites were used for Suzuki reaction [36]. In that study, PdCl₂ was used as Pd salt and this was loaded by using impregnation method. Two large-pore zeolites, namely faujasite (CsX, KX, KY) and BEA were used in their study. The prototypical Suzuki coupling of bromobenzene and phenylboronic acid was studied without adding any ligand as a test reaction to determine the activity of prepared catalysts. The highest yield was obtained in presence of 1% Pd containing Beta zeolite by using K₂CO₃ as a base at 50 °C for 24 h in ethanol. However, in aprotic solvents, such as ethanol there was significant Pd leaching. In addition to this, these reactions were carried out in the presence toluene and ethanol/water mixture. The yield of biphenyl in toluene using K₂CO₃ was only at moderate level.

In present study, Y type zeolite was used as catalyst support. First of all, Pd(OAc)₂ complex was adsorbed in the Y type zeolite and activity of this catalyst was examined with 4- iodoanisole or 4- bromoanisole (as an aryl halide) with phenylboronic acid (as an arylboronic acid). Since reusability property was not satisfactory for Pd(OAc)₂ loaded Y type zeolite, the study was continued with Pd(II) exchanged Y type zeolite.

The activity of Pd(II) Y type zeolite was examined by using various substituted aryl bromides with arylboronic acids.

Before covering the experimental methods, discussion of the results obtained in this study, much more detailed background on various C-C bond formation reactions and heterogeneous catalyst systems are given.

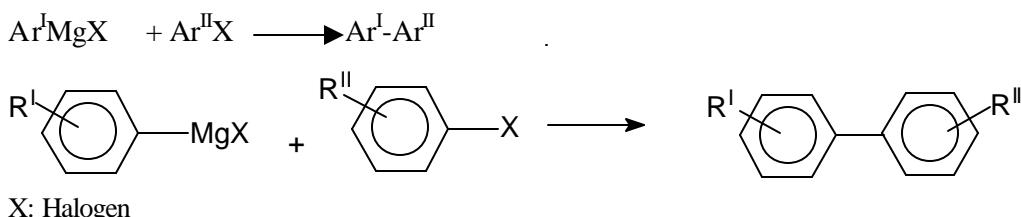
CHAPTER 2

2.1 SYNTHESIS OF BIARYL DERIVATIVES

Biaryls are of an important class of organic compounds. Natural products, polymers, advanced medicinal materials area interest in these biaryl derivatives. There are four main catalytic methods that are used for the synthesis biaryl derivatives. These are Kharasch, Negishi, Stille and Suzuki Reactions.

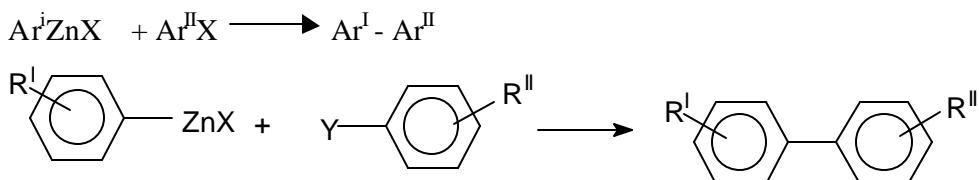
2.1.1. The Kharasch Reaction

The Kharasch reaction began to achieve importance as a method for biaryl synthesis in 1970's [1]. In this reaction type, Grignard reagents (Aryl magnesium halogen $\text{Ar}^{\text{I}}\text{MgX}$) generally react with aryl halides. ($\text{Ar}^{\text{II}}\text{X}$) in the presence of an appropriate catalyst (PdPh(PPh)_3 , Pd(dppb)Cl_2 , NiCl_2 , Ni(dppe)Cl_2) to yield biaryl structure.



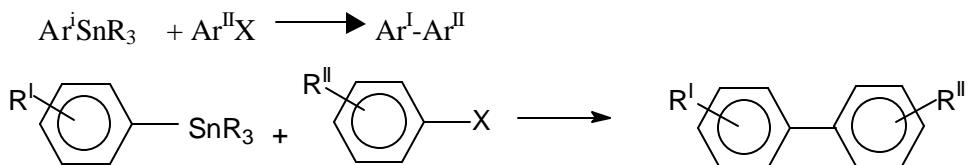
2.1.2. The Negishi Reaction

The Negishi reaction utilizes aryl zinc reagent ($\text{Ar}^{\text{i}}\text{ZnX}$) and aryl halides ($\text{Ar}^{\text{II}}\text{X}$). This reaction began to achieve importance in the mid 1970's [1].



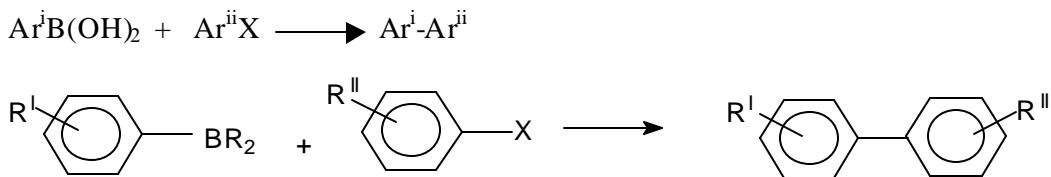
2.1.3. The Stille Reaction

In Stille Reaction aryl tin ($\text{Ar}^{\text{I}}\text{SnX}_3$) compounds are reacted with aryl halides ($\text{Ar}^{\text{II}}\text{X}$) to synthesize biaryl derivatives. This reaction has been familiar only since 1977 [1].



2.1.4. The Suzuki Reaction

Organoboron derivatives and aryl halides are used to synthesize biaryl compounds in the Suzuki Reactions. This reaction is a more important type C-C bond formation reaction than the reactions described above. The Suzuki coupling reactions have the most popularity because of the ready availability of a wide variety of functionally substituted organoboron derivatives and mildness of the coupling reaction itself and also organoboron reagents are easily accessible, stable in air and inert to various functional groups.



2.2. THE IMPORTANCE OF SUZUKI COUPLING REACTIONS

When the coupling reactions of organoboron compounds with aryl, alkenyl and alkynyl halides are performed these reactions are called the Suzuki reactions or Suzuki Miyaura coupling.

The characteristic feature of boron chemistry is different than that of other organometallic reagents. The B-C bond is observed to be almost completely covalent and organic groups on boron are weakly nucleophilic, thus limiting the use of such organoborone reagents for ionic reactions. The coordination of negatively charged bases to the boron atom has been recognized to be an efficient way of increasing its

nucleophilicity to transfer the organic group on boron to the adjacent positive centre. The cross coupling reaction of organoboron compounds with organic halides in the presence of a catalytic amount of palladium complexes and bases has been found to proceed smoothly and such a reaction has proved to be quite a general technique for a wide range of selective carbon–carbon bond formation. Many organometallic reagents undergo similar cross-coupling reactions, but much attention has been focused recently on the use of organoboronic acids in the laboratories and industries, because they are convenient reagents that are generally thermally stable and inert to water and oxygen, thus allowing their handling without special precautions. On the other hand, these boron compounds after the reactions can be handled and disposed more easily than Zn and Sn compounds used for similar cross-coupling reactions. For these reasons, the boron method is superior to Zn and Sn methods in coupling a commercial scale [37].

2.3. TRANSITION METAL REAGENTS

Transition metal complexes formed by the coordination of ligands (L) to metals are used for synthetic reactions. The transition metal itself is used rarely. The change of properties of transition metals, brought about by complex formation, is considerable. Such that Pd is a stable noble metal and its' complex $\text{Pd}(\text{Ph}_3)_4$ is greenish-yellow crystals and soluble in organic solvents. The stoichiometry of complex formation can be understood by the 18-electron rule. According to this rule a stable complex with an electron configuration of the next highest noble gas is obtained when the sum of d electrons of metals and electrons donated by ligands equals 18. Complexes that obey the 18-electron rule are said to be coordinatively saturated.

When a reaction of an organic compound (either promoted or catalysed by transition metal complexes) occurs, the reactant must coordinate to the metal [38].

2.4. WHY PALLADIUM AS A CATALYST IN ORGANIC REACTIONS ?

There are several features, which make reactions involving Pd particularly useful and versatile among many transition metals used for organic synthesis. Most importantly, Pd offers many possibilities of carbon-carbon bond formation. The importance of carbon-carbon bond formation in organic synthesis needs no explanation, and no other

transition metals can offer such versatile methods for carbon- carbon bond formation as Pd. The tolerance of Pd reagents to many functional groups such as carbonyl and hydroxyl groups is an additional important feature. Pd-catalysed reactions can be carried out without protection of these functional groups. Although reactions involving Pd should be carried out carefully, Pd reagents and catalyst are not very sensitive to oxygen and moisture, or even to acids. On the other hand, in many reactions catalysed by Pd-phosphine complexes, it is enough to apply precautions to avoid oxidation of the phosphine, and this can be done easily.

Of course, Pd is a noble metal and expensive, but it is much less expensive than Rh, Pt, and Os. Also, the toxicity of Pd has posed no problem so far. The fact that a number of industrial processes (more than ten at least) based on Pd catalysed reactions have been developed and are now operated reflects these advantages of using Pd catalyst commercially [37].

2.5. MECHANISM OF SUZUKI COUPLING REACTIONS

The mechanism of the Suzuki coupling reactions consists of four main steps (Figure 2.1):

- Oxidative addition of aryl halides to palladium catalyst
- Transmetalation of aryl borate to form trans -diaryl palladium complex
- Trans -cis isomerization of this palladium complex
- Reductive elimination of the biaryl to regenerate the catalyst.

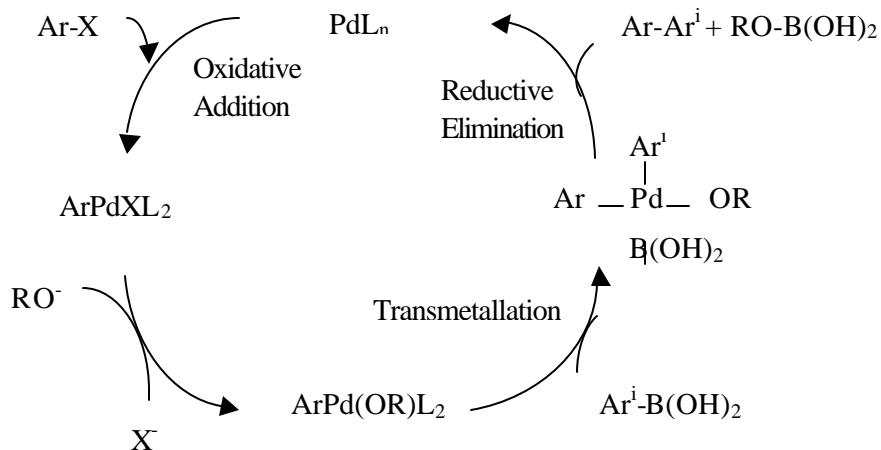


Figure 2.1. General Mechanism of Suzuki Coupling Reactions [39].

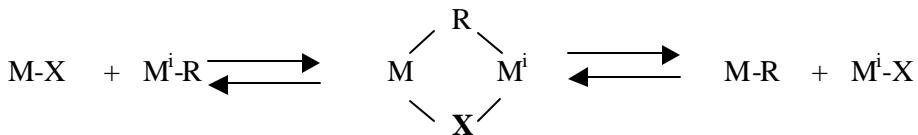
2.5.1. Oxidative Addition

The term “oxidative” may sound strange to organic chemists who are not familiar with organometallic chemistry. The use of this term in organometallic chemistry has a meaning different from the “oxidation” used in organometallic chemistry, such as the oxidation of secondary alcohols to ketones. Thus oxidative addition means the reaction of a molecule X-Y with a low valent coordinatively unsaturated metal complex $\text{M}_{(n)}\text{L}_m$ to undergo bond cleavage and form two new bonds. As two previously nonbonding electrons of the metal are involved in the new bonding, the metal increases its formal oxidation state by two units, namely, $\text{M}_{(n)}$ is oxidized to $\text{M}_{(n+2)}$, and increases the coordination number of the metal centre by two. In oxidative addition, it is defined that the electrons in the two new bonds belong to the two ligands, and not to the metal [38].



2.5.2. Transmetallation

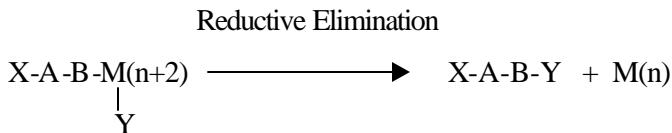
In this reaction one metal replaces the other metal, which is in the complex.



M is more electropositive than Mⁱ metal. So one metal replaces the other metal, which is less electropositive, in this reaction [38].

2.5.3. Reductive Elimination

Similar to “oxidative” the term “reductive” used in organometallic chemistry has a meaning different from reduction in organic chemistry. Reductive elimination is a unimolecular decomposition pathway and the reverse of oxidative addition. Reductive elimination involves the loss of two ligands from the metal centre, which is shown in below.



By reductive elimination, both the coordination number and the formal oxidation state of the metal M(n+2) are reduced by two units to generate M(n) [38].

2.6. FACTORS AFFECTING THE SUZUKI COUPLING REACTIONS

Several parameters affecting the Suzuki coupling reactions are considered. These factors are; solvent effect, substitution group effect, halogen effect and ligand effect.

2.6.1. Solvent Effect

Solvents are the most important parameters in organic reactions. As in general organic reactions, appropriately chosen solvent system strongly favours the cross coupling pathway. In literature, THF, different DMA/H₂O, DMF/H₂O and EtOH/H₂O ratios, toluene and benzene have been used as solvents in Suzuki Coupling reactions.

2.6.2. Substitution Group Effect

In Suzuki coupling reactions substituent are the most important to influence the activity of the reaction. These groups substantially influence the activity of aryl halide. The reaction is promoted, when electron-withdrawing groups substitute aryl halide. In Suzuki coupling reaction mechanism, first step involves carbon halide bond cleavage.

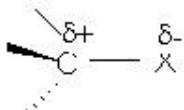
Carbon halide bond cleaves more easily when it substitutes with electron withdrawing groups (NO_2 , CF_3 , CN , etc.) and thereby the reaction proceeds faster as the C-X bond is weakened. This bond will be broken easily and reaction will be faster. (See the mechanism of Suzuki-coupling reaction given in Figure 2.1.)

In contrast, if this aryl halide group contains an electron donating group (CH_3 , OCH_3 etc) carbon halide bond will be stronger. So bond cleavage will be more difficult and reaction would probably proceed slower [40].

2.6.3. Halogen Effect

The halogen type also determines the activity of aryl halide towards the Suzuki reaction. The strength of the carbon-halogen bond depends on the electronegativity of the halogen.

Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of aryl halides is polarized. As a result of this the carbon atom bears a partial positive charge and the halogen atom bears a partial negative charge.



The size of the halogen atom increases as we go down the periodic table. Fluorine atom is the smallest and iodine atom is the largest. The carbon-halogen bond length also increases as we go down the periodic table [40].

So, in Suzuki reactions, when palladium is used as catalyst, oxidative addition of palladium into a carbon-halogen bond occurs in the order of $\text{I} > \text{Br} >> \text{Cl} >> \text{F}$, based mainly on the strength of the carbon-halogen bond.

2.6.4. Ligand Effect

In homogeneous Pd catalysed Suzuki reactions, generally phosphine ligands have been used to promote the reactions. The electronic properties of the ligand are certainly of

importance. If a ligand is not sufficiently electron rich to promote the oxidative addition of aryl halide, the reaction rates will be slower.

In this study, to investigate the ligand effect, $\text{PPh}(\text{CH}_3)_2$ and 3-methylbenzothiazolium iodide was used.

2.6.5. Base Effect

Suzuki coupling reaction proceeds via transmetalation in the presence of bases. This procedure does not take place under neutral conditions. This is a characteristic feature of boron chemistry, which is different from that of other organometallic reagents. The most commonly used base in the Suzuki cross coupling reaction is Na_2CO_3 but this is often ineffective with sterically demanding substrates. In such instance, $\text{Ba}(\text{OH})_2$ or K_3PO_4 has been used to generate good yields of the cross coupling products. Other bases utilised in the Suzuki cross coupling reaction include Cs_2CO_3 , K_2CO_3 , TlOH , KF and NaOH . It is known that the base is involved in the coordination sphere of the palladium and the formation of the $\text{Ar-PdL}_2\text{-OR}$ from $\text{Ar-PdL}_2\text{-X}$ is known to accelerate the transmetalation step. (Figure 2.1.) [41].

CHAPTER 3

CATALYSIS

BACKGROUND: CATALYSIS AND ZEOLITE CHEMISTRY

3.1. INTRODUCTION

Various older definitions of the term “catalysis”, though they continue to be used in part of the scientific literature, are nowadays considered less appropriate. A scientifically sound definition of a catalyst describes it as a substance which transforms reactants into products via an uninterrupted and repeated cycle of elementary step in which the catalyst participates while being regenerated in its original form at the end of each cycle during its life.

The incentives for using a catalyst for a desired chemical reaction can be manifold. Catalysis is often very useful if an endothermic reaction is to be performed. In this case, high temperature would be advantageous for the reaction kinetics, but in many instances high temperature shifts the thermodynamic equilibrium towards undesired direction. At the same time reducing the reaction temperature would decrease the rate of the chemical reaction. In this situation, using a catalyst efficiently accelerates the reaction and increases the reaction rate at low temperature.

High reaction temperature would be advantageous for both the position of the thermodynamic equilibrium and reaction rates in an endothermic reaction. In this situation, using a catalyst helps to conduct the desired reaction at lower temperature with reasonable rate. For this reason, in organic reactions, homogeneous and heterogeneous catalysts are used [42].

3.2. HOMOGENEOUS CATALYSTS

In homogeneous catalysis the reactants, product and catalyst are all in the same phase. Often the reactants, products and catalyst are all dissolved in the same phase. Generally palladium catalysts in Suzuki coupling reactions are carried out in homogeneous system

according the literature. But in this system highly expensive palladium complexes, which is so important for industrial application, are not regenerated, recovered, and separated. In addition to the separation problems, deactivation of the homogeneous catalyst by formation of inactive colloidal species is encountered at the comparatively high temperatures. Thereby homogeneous catalysts cannot be reused in general.

Various heterogeneous catalysts, such as Pd/C, Pd/MgO, Pd/Al₂O₃, Pd/SiO₂ and Pd/Zeolite, catalysts have been used in various C-C bond formation reactions. This thesis aimed of studying first use of Pd(II) exchanged NaY zeolite for the Suzuki cross-coupling reactions of aryl halides with arylboronic acids.

3.3. ZEOLITES AS HETEROGENEOUS CATALYSTS AND SUPPORT MATERIALS

Zeolites exist in nature and have been known since almost 250 years as aluminosilicate minerals. Most common examples are clinoptilolite, faujasite, mordenite, ferrierite and chabazite. Today most of these and many other zeolites are of great interest in many fields. Out of these fields, catalysis is the most essential application of zeolites in terms of financial market size, but not in terms of tons of production per year [42].

These aluminosilicate minerals have been used as heterogeneous catalyst for their four main properties. These are;

1. They have exchangeable cations allowing the introduction of cations with various catalytic properties.
2. If these cationic sites are exchanged to H⁺, they can have a very high number of very strong acid sites.
3. Their pore diameters are less than 10 Å.
4. They have pores with one or more discrete sizes.

In addition, there are several important properties of zeolite catalyst that are not found in traditional amorphous catalyst. These can be listed as follows:

1. Zeolites have porous crystal structures made up of channels and cages that allow a large surface area thus a large number of catalytic sites. Zeolites can accommodate as many as 100 times more molecules than the equivalent amount of amorphous catalyst.
2. Zeolites are strong acid catalyst due to a large proportion of Bronsted acid sites scattered throughout their porous structure.
3. Since they are solid, they are easily removable from products and therefore they are environmentally benign.
4. Furthermore their molecular sieve action can be exploited to control, which molecules have access to or which molecules can depart from the active sites, which is defined as shape selectivity.

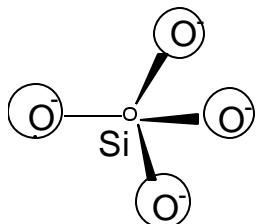
But unfortunately from the catalytic point of view, their naturally occurring forms are of limited value, because [43]

1. They almost always contain undesired impurity phases.
2. Their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit and
3. Nature did not optimise their properties for catalytic application.

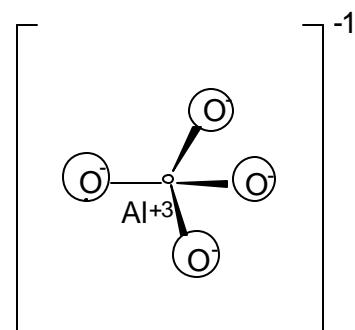
3.4. ZEOLITE CHEMISTRY

3.4.1. Chemical Structure

Zeolite comprises a three-dimensional crystal network of Si and Al atoms are present in the form of SiO_4 and $[\text{AlO}_4]^{-1}$ tetrahedra.



Silica Tetrahedron



Alumina tetrahedron

Tetrahedral units join together through shared oxygen atoms with various regular arrangements, to form hundreds of different three-dimensional crystal frameworks (Figure 3.1).

The zeolite framework contains channels, channel intersections and/or cages with dimensions between 0.2 nm and 2 nm. Inside these voids are water molecules and small cations [43]. Since the trivalent aluminum is bonded to four oxygen anions, each AlO_4 tetrahedron in the framework bears a net negative charge, which is balanced by a cation, generally from the group IA or IIA [44].

The silica and alumina tetrahedral are combined into more complicated secondary units, which form the building blocks of the framework zeolite crystal structure. The silica and alumina tetrahedra are geometrically arranged, with Al-O-Al bonds excluded. The unit cell formula is usually written as $M_{n^+}[\text{AlO}_2]_x(\text{SiO}_2)_y\text{zH}_2\text{O}$, where M_n^+ is the cation, which balances the negative charge, associated with the framework aluminum ions. These metal cations, which neutralize the excess anionic charge on the aluminosilicate framework, are usually alkali metal and alkaline earth metal cations and at least some of them must be able to undergo reversible ion exchange if the material is to be classed as zeolite.

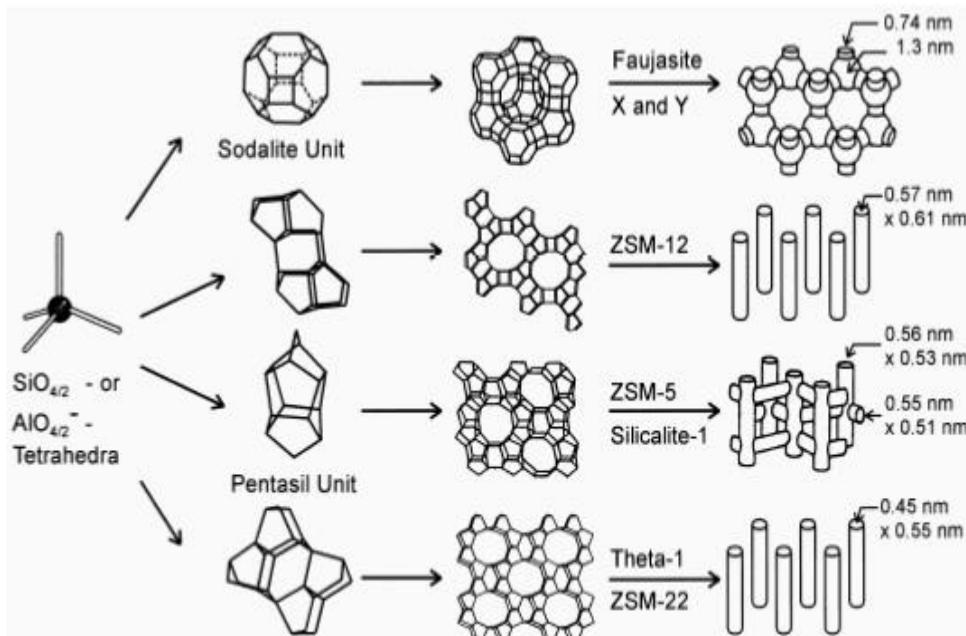


Figure 3.1. SiO_4 and AlO_4 building blocks of zeolites [43].

According to the increasing framework Si / Al ratio, zeolites are categorized as: (i) low Si / Al zeolites (1 to 1.5, zeolite A, zeolite X); (ii) intermediate Si / Al zeolites (~ 2 to 5, mordenite); (iii) high Si / Al zeolites (~ 10 to 100, ZSM-5, Beta); and (iv) silica molecular sieves (silicalite-1). As the Si / Al ratio of a zeolite increases, its cation content decreases, its thermal stability increases, and its surface selectivity changes from hydrophilic to hydrophobic. Silica molecular sieves (silicalite-1) have a neutral framework, are hydrophobic in nature, and have no ion exchange or catalytic properties, since $[AlO_4]^{-1}$ tetrahedra do not exist in the framework structure [44].

3.5. ACIDITY AND BASICITY OF ZEOLITE

The replacement of SiO_4 tetrahedra by the $[AlO_4]^{-1}$ tetrahedra in the zeolite framework results in excess negative charge that needs to be neutralized by cations. Compensation of the negative charge by associated cations like H^+ , Na^+ , K^+ , Ca^{+2} , and NH_4^+ generates the acid sites. The catalytic activity of the zeolites is attributed to the existence of these acidic sites and the proton affinity at the charged framework. The catalytic activity of acid sites is either Bronsted or Lewis in character [45]. If the acid site is of Bronsted type, it acts as a proton donor. If the acid site is of Lewis type, it acts as an electron acceptor.

The charge compensating cation associated with the tetrahedral aluminum is ammonium, heating the zeolite between 300-400 °C would cause the zeolite surface obtain the capacity to act as a proton donor and therefore act as a Bronsted acid. If the zeolite is heated to a temperature higher than 450°C, the formation of Lewis acid site and zeolitic water would occur [43]. Ward proposed that two Bronsted acidic sites are needed for the formation of a single Lewis (electron acceptor) acidic site (Figure 3.2.) [46].

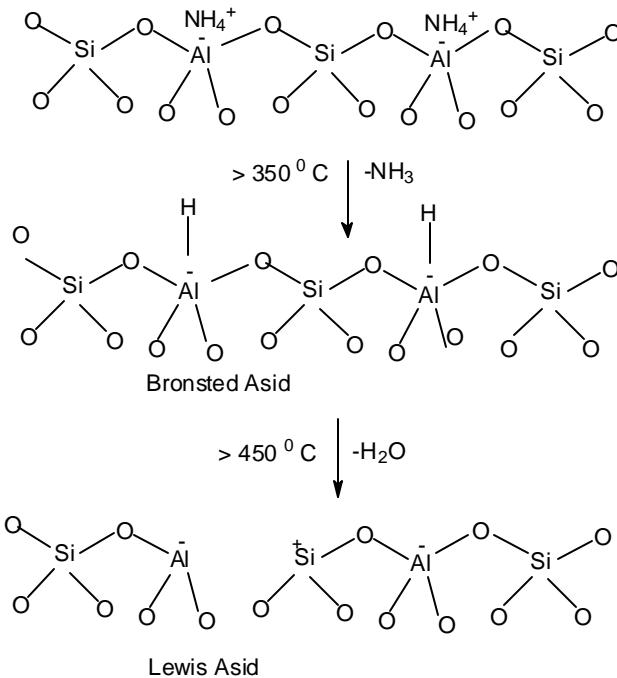


Figure 3.2. Bronsted and Lewis Acid Site Formation

At the same time some reactions occur in the basic solution. In this situation zeolite could be used as basic catalyst. Basic catalysts are prepared by several methods. These are;

- i. exchange of the zeolite with basic cations (K^+ , Rb^+ , Cs^+)
- ii. deposition of basic oxides (MgO) or by
- iii. synthesis of metallic clusters inside the zeolite cages.

3.6. PORE STRUCTURE AND MOLECULAR SIEVING

There are mainly two types of pore structures of zeolites. One of them provides an internal pore system comprised of interconnected cage-like voids, e.g. Zeolite A and Zeolite Y. The other one provides a three dimensional system of uniform channels, e.g. ZSM-5 has set of straight parallel pores intersected by a set of perpendicular zigzag pores or a one-dimensional channel system composed of only straight parallel pores as in ZSM-22 (Figure 3.1.).

The diameters of the windows or pore leading into the voids vary from 3 to 13 Å according to the arrangement of the tetrahedral units. The size of aperture depends on

the number of oxygen atoms present in the ring. The apertures can have 8, 10, or 12 oxygen atoms and zeolites are classified according to this number of oxygen atoms as 8, 10, or 12 oxygen membered ring zeolites. The size of the aperture is also dependent on the sizes of nearby cations, which may partially block it.

Zeolite Y is of outmost importance in heterogeneous catalysis, for example it is the active component for fluid catalytic cracking. Their pore systems is relatively spacious and consist of spherical cages, referred to as supercages, with a diameter of 1.3 nm connected tetrahedrally with four neighbouring cages through windows with the diameter of 0.74 nm formed by 12 TO_4 -tetrahedra. Zeolite Y is therefore classified to possess a three-dimensional, 12 membered-ring pore systems [43]. The Al ions in the unit cell of zeolite Y vary from 76 to 48.

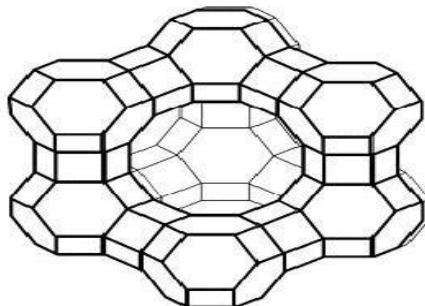


Figure 3.3. Schematic presentation of the cage system of zeolite Y

($\text{SiO}_2/\text{Al}_2\text{O}_3$: 5.2, Unit Cell Size: 24.53 Å, Surface Area: $750\text{m}^2/\text{g}$, Channel Size: 7 Å
Cage Size: 13 Å)

3.7. SHAPE SELECTIVITY

As acidic, basic, or redox catalysts, zeolites essentially act in a way similar to their homogeneous counterparts. However, because of their specific nature, these solid microporous materials sometimes show a behaviour not observed in the homogeneous phase. Shape selectivity of zeolites is such kind of a behaviour.

In zeolites, most of the active sites are located in the well-defined and molecularly sized pores and cages. Throughout a reaction, the transforming molecules are continuously exposed to steric limitations imposed by the zeolite structure, possibly changing the course of the reaction and finally resulting in product distributions showing deviations

from those obtained in the homogeneous phase. In this context, molecular shape selectivity can be described as the restrictions imposed on guest molecules by size and shape of the zeolite pores. There are three types of molecular shape selectivity observed associated with zeolites [42]:

- 1) Reactant selectivity** implies that those molecules with high diffusivity will react preferentially and selectively, while molecules excluded from the zeolite interior will only react on the external surface of the zeolite.

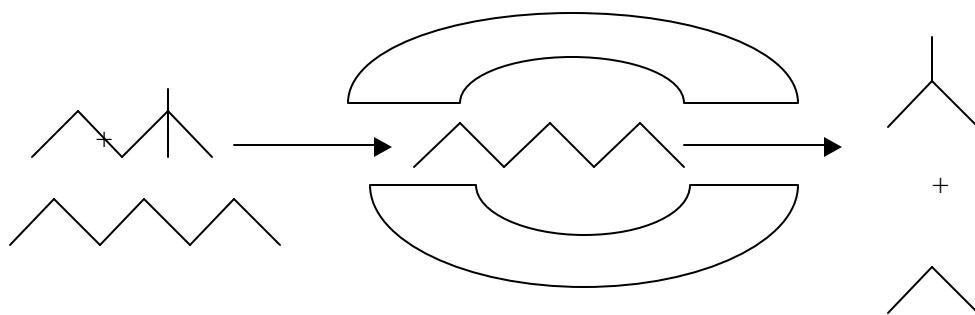


Figure 3.4. Reactant Selectivity

- 2) Product selectivity** implies that products with high diffusivity will be preferentially desorbed, while the bulkier molecules will be converted and equilibrated to smaller molecules, which will diffuse, or eventually react to form larger species, which will block the pores.

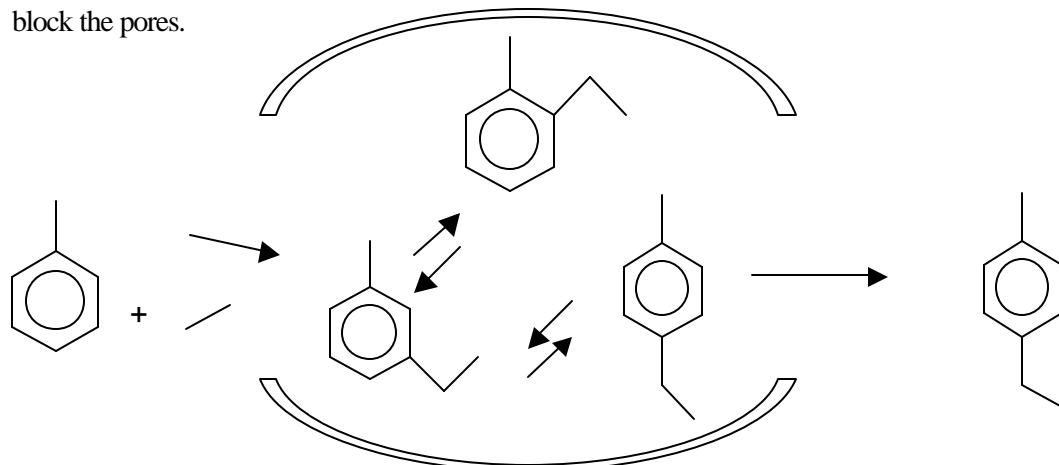


Figure: 3.5. Product Shape Selectivity

3) Transition state selectivity takes place when certain reactions are prevented, as the transition state necessary for them to proceed is not reached because of the space restrictions.

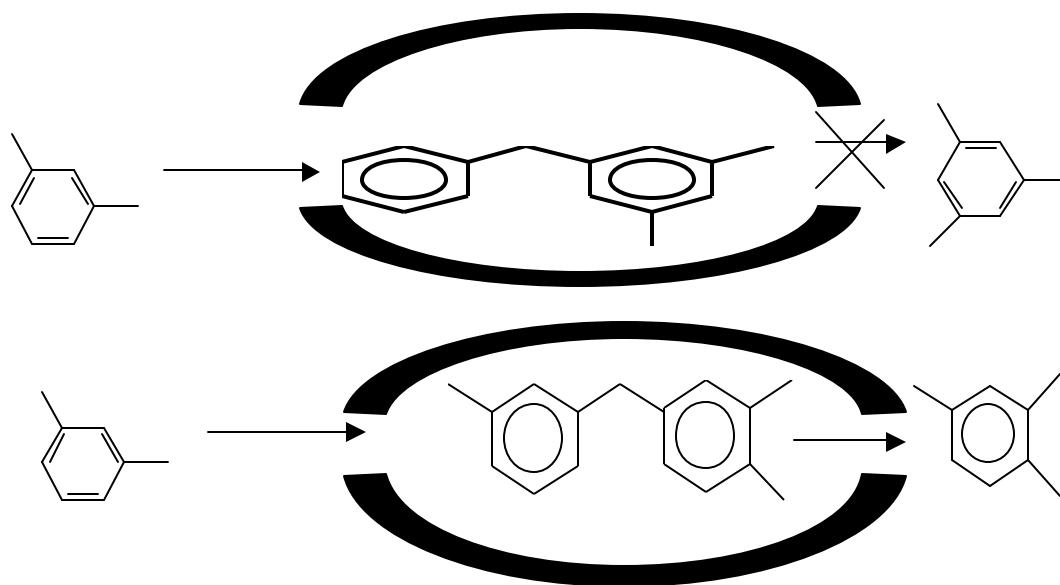


Figure 3.6. Transition State Selectivity

Modification of the shape selective properties of zeolites is possible with different approaches for catalytic purposes. Most of these approaches do not only change the shape selectivity but also the acid properties of zeolites. It is in fact impossible to change these properties independently. These approaches are given as follows:

- (i) Cation exchange: Small cations like H^+ and Na^+ can be replaced by larger cations such as K^+ , Rb^+ , Cs^+ , using the ion-exchange method. This replacement results in the narrowing of the pore diameter of the zeolite channels in addition to a change in the number and strength of the Bronsted acid sites.
- (ii) Deposition of inorganic oxides: By deposition of inorganic oxides in the pores of the zeolite, the effective pore diameter is reduced and the steric constraints on reactants, transition state or products are enhanced. Deposition of these oxides also changes the acidic and basic properties of the zeolite.

(iii) Crystal size: The crystal size of zeolite catalysts can be varied by adapting the synthetic conditions. By increasing crystal size, the fractional amount of sites on the outside of the crystal in comparison to the total amount of sites decreases and consequently the centre of catalytic activity shifts from extra to intrazeolitic.

(iv) Deactivation of the external surface: For small crystals, the active sites on the external surface largely contribute to the catalytic activity of the material. In the case of Bronsted acid sites, they can be deactivated by deposition of inorganic oxides or neutralized by chemical reaction with organosilanes, which are too bulky to diffuse through the intracrystalline voids. By silylation, the hydrophobicity of the materials is enhanced.

(v) Deposition of organic bases: Deposition of organic bases in the intracrystalline voids narrows the pore apertures and so enhances the steric constraints on molecular diffusion [42].

3.8. METAL ZEOLITE CATALYST

Supported metal catalysts are widely used in petroleum refining, chemical and petrochemical industries. These catalysts are important in ammonia synthesis, conversion of hydrocarbons with water vapour to synthesis gas, reforming, hydrocracking, hydrorefining, hydrodealkylation, hydrocyclisation, isomerization of ethylbenzene to xylenes, reduction of various organic compounds and so forth.

In these reactions metal-containing zeolites can be used as catalyst for different purposes and under various conditions. Therefore, their composition, preparation and activation depend on the process used.

Various techniques for preparation of catalyst can be employed, which are:

i. Ion Exchange Method

Zeolites, in a narrow definition, are porous crystalline aluminasilicates having a uniform pore structure and exhibiting ion-exchange behaviour. The framework of zeolite

consists of SiO_4 and AlO_4 tetrahedra sharing oxygen ions located at their apices, thus resulting in the general framework formula $(\text{AlO}_2)_x(\text{SiO}_2)_{(n-x)}$, where n is the number of tetrahedral per unit cell, and $x \leq n/2$. Since aluminum is trivalent, every AlO_2 unit carries a negative charge, which is compensated by a positive charge associated with a cation. Therefore, the ion-exchange capacity of a zeolite depends on the chemical composition. Higher ion exchange capacity is observed in zeolites of low $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio [42].

The cation exchange behaviour of zeolite depends upon

- i. the nature of the cation species, the cation size, both anhydrous and hydrated and cation charge,
- ii. the temperature,
- iii. the concentration of the cation species in solution,
- iv. the anion species associated with cation in solution,
- v. the solvent,
- vi. the structural characteristic of the particular zeolite

ii. Adsorption Method

Neutral metal compound is loaded into the zeolite by adsorption method. In this method neutral compounds solution treated with zeolite.

iii. Ship in Bottle Synthesis

Large zeolite cages offer themselves as locations for the synthesis of metal complexes with dimensions exceeding those of the pore apertures, so that they are trapped like a ship in bottle synthesis. The ship in bottle is used to immobilize such complexes within the zeolite cavities providing an opportunity to hydrogenise a homogeneous catalyst system.

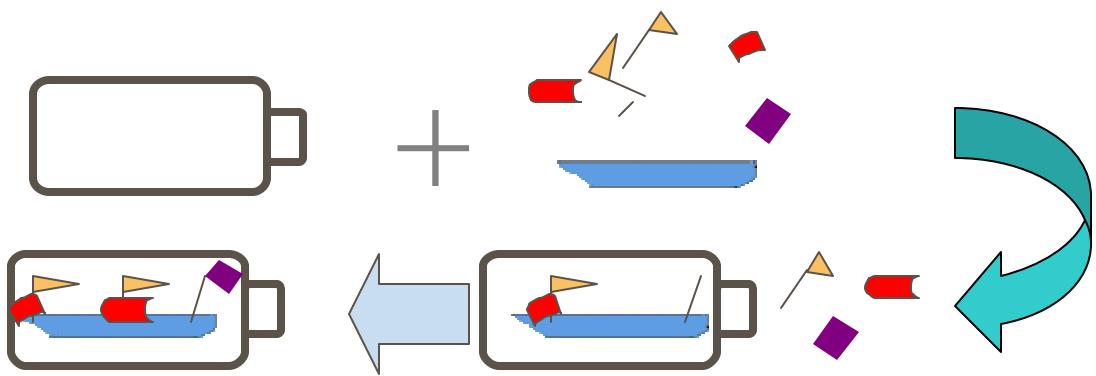


Figure 3.7. Ship in Bottle Synthesis

CHAPTER 4

EXPERIMENTAL STUDY

4.1. PREPARATION OF CATION EXCHANGED ZEOLITE

4.1.1. Preparation of Sodium Exchanged Zeolite

Sodium cations were loaded into the zeolite by stirring 25 g of NH₄Y zeolite (Zeolyst International, CBV 500, SiO₂/Al₂O₃ mole ratio: 5) in 250 mL 10 % NaNO₃ (Carlo Erba >99%) solution by refluxing over 24 h. The zeolite suspension was filtered, washed thoroughly by ultra pure water and this process was repeated three times. Sodium-exchanged zeolite was dried at 120°C after the ion-exchange process.

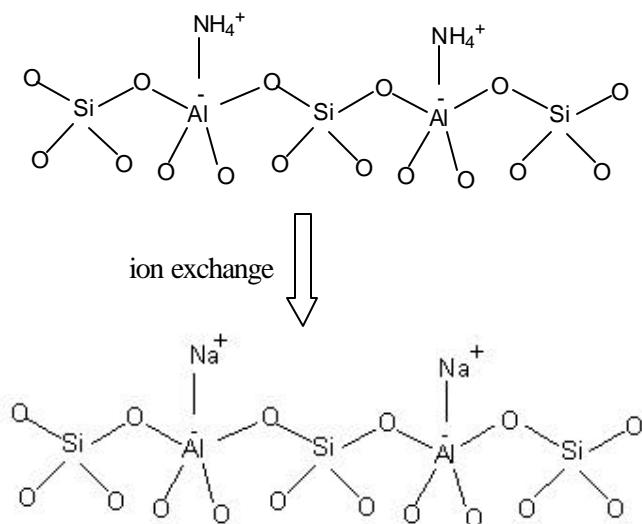


Figure 4.1. Sodium Exchanged NH₄Y Type Zeolite Structure

4.1.2. Preparation of Cesium Exchanged Zeolite

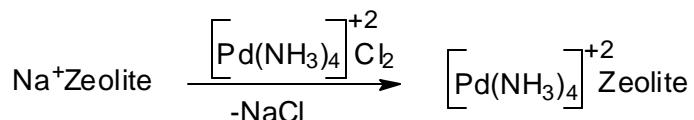
Cs⁺ cation was loaded into the zeolite by stirring 10 g of NH₄Y zeolite in a 50 mL solution of 0.3 M of cesium chloride (Merck, >99.5%) at 80 °C for 24 h. The zeolite suspension was filtered, washed thoroughly by ultra pure water and this process was repeated three times. Cesium exchanged zeolite was dried at 120 °C after the ion-exchange process.

4.2. PREPARATION OF PALLADIUM LOADED ZEOLITES

4.2.1. Preparation of $\text{Pd}(\text{NH}_3)_4^{+2}$ Modified Zeolite

$[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ complex was synthesized from PdCl_2 (Fluka, 47% purum) and excess NH_3 (Merck, 25%) solution. First of all NH_3 solution was added over PdCl_2 complex and some water was added drop wise to this solution while stirring. The solution colour turned to yellow from tobacco colour. This solution was boiled until all water was removed and yellow crystals were obtained. Then this complex was recrystallised with extra pure ethanol (Riedel , 95%).

Prepared $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ complex was solved in 0.1 M ammonia solution (1mL/g zeolite) and this solution was added drop wise to the suspension of NaY zeolite, which was calcinated at 400 °C for 10 hours under air atmosphere, in ultra pure water (100mL/g zeolite). The mixture was stirred for 24 h at room temperature and the exchanged zeolite was filtered off and washed until no trace of chloride was detected in the filtrate (AgNO_3 test). Then the zeolite was allowed to dry at room temperature to give entrapped $[\text{Pd}(\text{NH}_3)_4]^{+2}\text{Y}$ zeolite as a slightly yellow material. This procedure is showed that in Figure 4.2.



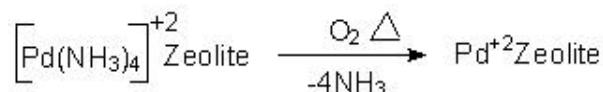
Scheme 4.1. Preparation of $\text{Pd}(\text{NH}_3)_4\text{Y}$ catalyst from NaY zeolite

4.2.2. Preparation of $\text{Pd}(\text{OAc})_2$ Modified Zeolite

A solution of $\text{Pd}(\text{OAc})_2$ (Fluka, 60% purum, 105 mg, 0.47 mmol, 1% Pd in the final catalyst) in THF (Merck, extra pure) (20 mL/g zeolite), which was dried with Na metal under argon and then distilled, was added drop wise to a suspension of NaY (5 g in 100 mL THF) or CsY which was calcinated at 400 °C for 10 h. The mixture was stirred for three days under argon atmosphere and the $\text{Pd}(\text{OAc})_2$ loaded zeolite was filtered and washed with THF until no trace of non-immobilized complex was detected in the filtrate. Then the zeolite were allowed to dry and stored under argon atmosphere.

4.2.3. Preparation of Pd(II) Modified Zeolite

The Pd(II) exchanged zeolite was obtained by calcinations of the entrapped $[Pd(NH_3)_4]^{+2}$ zeolite in a vertical type reactor under a pure oxygen flow (200 mL/min) according to following temperature program: The increase in temperature begun at 80 °C, then increased to 500 °C using a heating rate of 1 °C/min. The temperature was maintained at 500 °C for 2 hours and the reactor was cooled to room temperature under the flow of oxygen to give the Pd(II)Y catalyst. This Pd(II) loaded zeolite has a pink colour and it was stored in a desiccators.



Scheme 4.2. Preparation of Pd(II)Y catalyst from $Pd(NH_3)_4Y$ catalyst

4.3. CATALYST CHARACTERIZATION

The effect of the different pretreatments on the Pd catalyst can be followed by UV-vis diffuse reflectance spectroscopy (Cary 50 Varian) and by X-ray diffraction (Phillips Expert Pro), which may give information on the oxidation and coordination state of Pd.

4.3.1. UV Absorption of Palladium Loaded Y Type Zeolite

UV absorption spectra were taken to confirm the presence of $Pd(NH_3)_4^{2+}$ and Pd(II) which were loaded into the zeolite. First of all, oval quartz cells were covered with tetradecane and then zeolite samples were placed between these cells.

4.4. DETERMINATION OF Pd AMOUNT IN THE ZEOLITE

The palladium content of the catalyst was determined by atomic absorption spectroscopy (Solaar AASpectrometer Thermo Elemental). The dissolved zeolite samples were prepared according to the microwave digestion method, which is summarized below, for palladium content analysis,:

A mixture of 3 mL concentrated HNO_3 (Merck, 65%), 2 mL concentrated HCl (Merck, 37%), and 3 mL HBF_4 (Riedel, 48%) (tetrafluoroboronic acid) were added over 100 mg

of a zeolite sample and these mixtures were heated in the Ethos Plus Microwave Labstation furnace according to the following heating program: Mixtures were heated to 180 °C in 5 minutes under 600 W power. In the next step, they were hold at 180 °C for 10 minutes under 650 W powers. At the end of this program, the solutions were diluted approximately to 1:20. Palladium containing standard solutions (1, 2, 3, 4, 5 ppm) were prepared from standard solution (0.5 mol/L) of 1000 ppm Pd(NO₃)₂ in nitric acid for AAS analysis.

4.5. SUZUKI COUPLING REACTIONS

The Suzuki reactions were carried out in a 50 mL round-bottom flask connected to a condenser in an oil bath or at room temperature under argon atmosphere. The palladium loaded catalyst was added into the flask. Over this, 1 mmol aryl halide, 1.2 mmol arylboronic acid and base in succession. 0.6 mmol internal standard were added (when Pd(OAc)₂ loaded NaY was used, solvent mixtures contained 0.6 mmol dodecane (Merck, >99%) as an internal standard. When Pd(II) loaded NaY was used 0.6 mmol tetradecane (Merck, >99%) and hexadecane (Merck, 99,5%) were used as internal standards and these were added in to the reaction mixtures after the reaction). The reaction was started by the addition of 10 mL DMF: H₂O mixtures.

Heterogeneous catalyst was separated by suction filtration at the end of reactions. The catalyst was washed several times with dichloromethane to remove organic materials from zeolite cages. Organic phase was separated from water with dichloromethane and dried with Na₂SO₄. Aliquots of samples were taken analysed by GC and GC/MS techniques.



Figure 4.2. Experimental set-up designed for the Suzuki coupling reactions

4.6. GC METHOD

The samples were analysed by GC/MS (Varian Star 3400CX/Varian Saturn 2000, DB5, 30 m, 0.25 mm column) and GC (Shimadzu GC-17A on a 30-m capillary column and with a FID detector). The GC and GC/MS programs applied throughout the analysis was as follows: the column temperature was 40 °C at the beginning of the program and it was heated with a rate of 5 °C/min up to 100 °C, then it was heated with a rate of 2 °C/min up to 120 °C and then it was heated with a rate of 6 °C/min up to 250 °C. Throughout the analysis the injector and detector temperatures were kept constant at 280 °C and 300 °C, respectively. The analysis was performed on 1/50 split mode. A sample of gas chromatogram of a reaction product according to this temperature program is given in Figure 4.3. The gas chromatogram and mass spectra of some biphenyl products are given in Figure 4.4, Figure 4.5, Figure 4.6. and Figure 4.7.

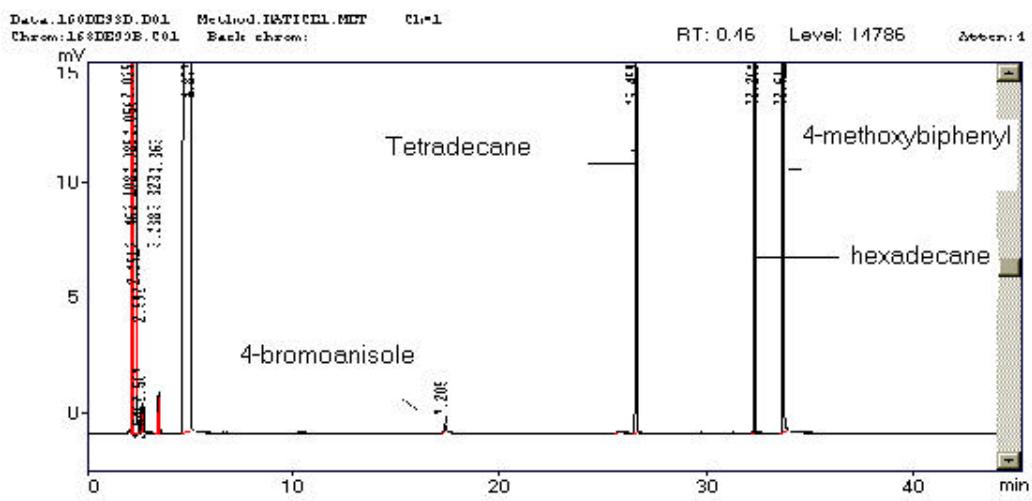
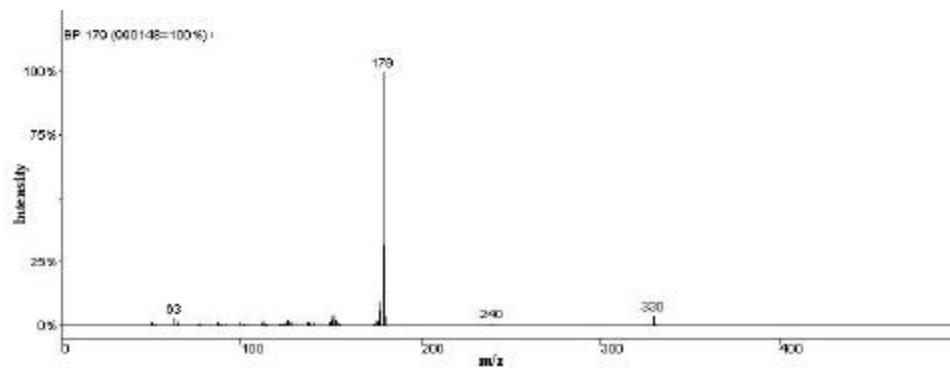
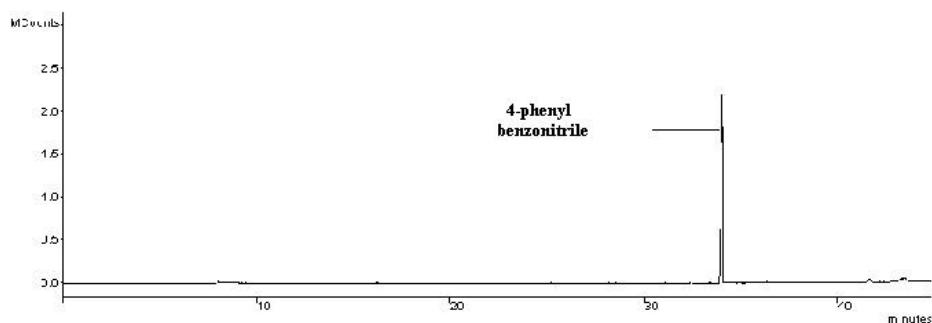


Figure 4.3. Gas chromatogram of a reaction product

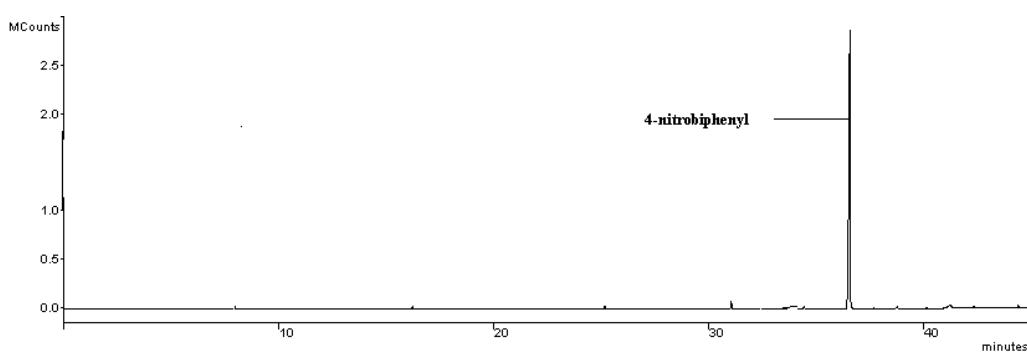
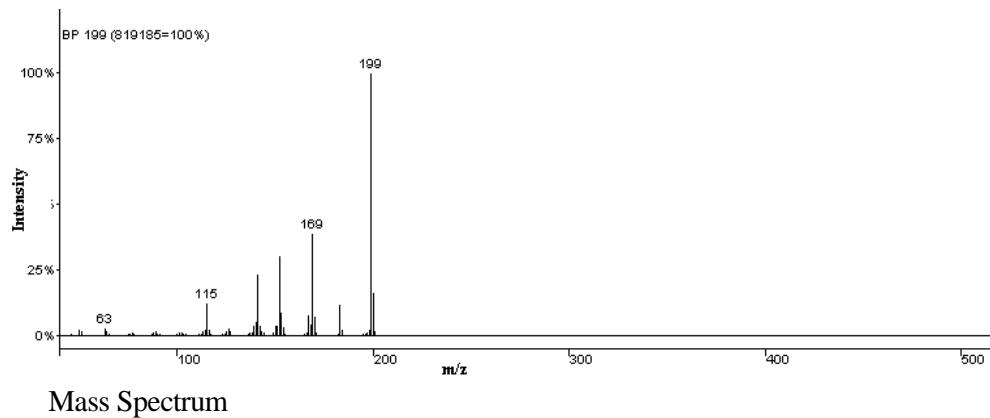


Mass Spectrum



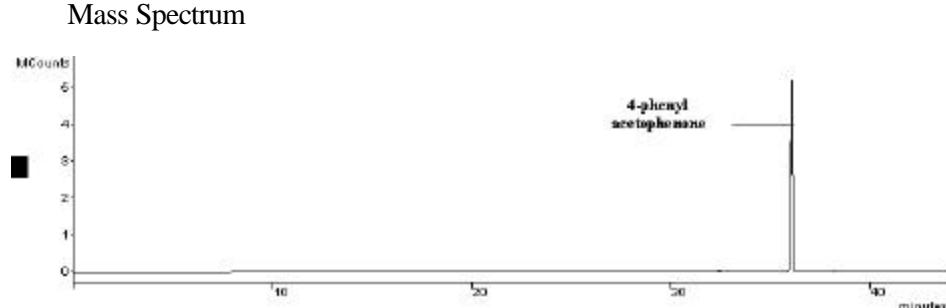
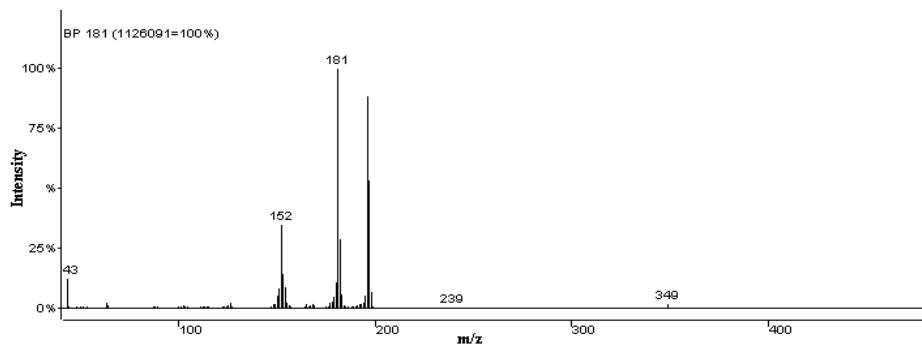
Gas Chromatogram

Figure 4.4. GC/MS of 4-phenyl benzonitrile



Gas Chromatogram

Figure 4.5. GC/MS of 4-nitrobiphenyl



Gas Chromatogram

Figure 4.6. GC/MS of 4-phenyl acetophenone

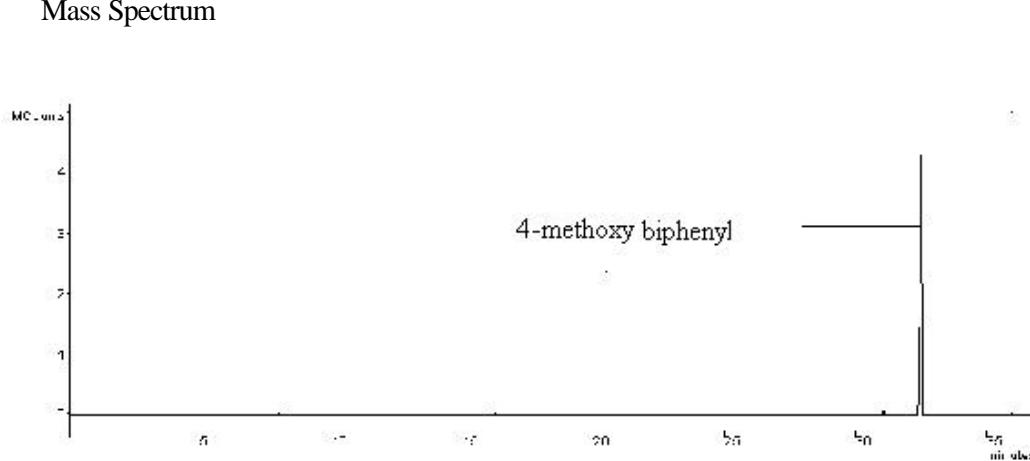
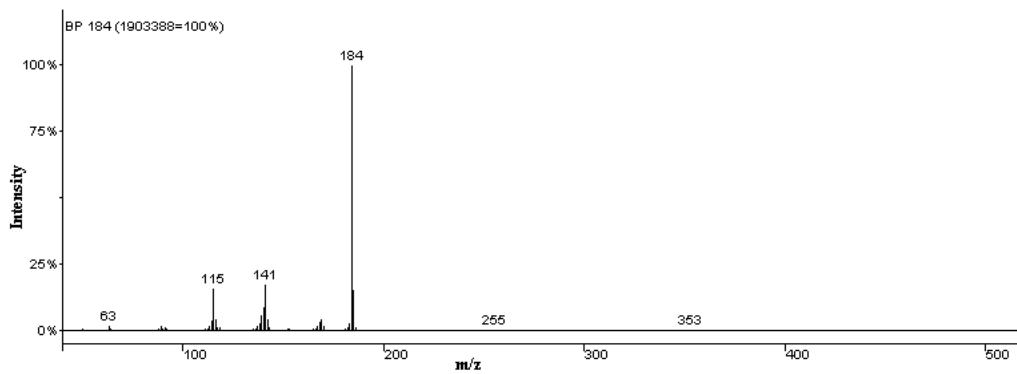


Figure 4.7. GC/MS of 4 methoxy biphenyl

4.7. CALCULATION OF REACTANT AND PRODUCT AMOUNT ON GC

The response factor of each reactant and product for the set temperature program of GC was determined for the calculation of the amount of reactants and products. As internal standard, dodecane was used with experiments which were done with $\text{Pd}(\text{OAc})_2$ loaded Y type zeolite, tetradecane and hexadecane were used in the experiments which were done with Pd(II) loaded Y type zeolite. The amount of internal standard did not change throughout the reaction, so the response factor of each compound was determined according to the amounts and areas under the peaks of internal standard and standard compound of interest. A known amount of standard compound together with a known amount of internal standard was dissolved in the reaction solvent and it was diluted with dichloromethane and then injected to GC for the determination of response factor of a compound. After the analysis was completed according to the set temperature program. The following equation is used for the determination of response factor of the compound:

$$R.F. = \left(\frac{\text{int. st. area}}{\text{compound area}} \right) \times \left(\frac{\text{compound amount}}{\text{int. st. amount}} \right) \quad (4.1.)$$

$$\text{amount of compound} = \left(\frac{\text{int. st. amount}}{\text{int. st. area}} \right) \times R.F. \times \text{compund area} \quad (4.2.)$$

4.8. PURIFICATION OF THE BIARYL DERIVATIVES

Various types of products were purified by using column chromatography or crystallization techniques in this study.

The reaction mixture, which contained biaryl derivatives were separated from catalyst by filtration. Then the catalyst was washed with dichloromethane and aqueous phase was extracted. The organic phase was dried over sodium sulphate and solvents were removed by using evaporator. The product was purified by using column chromatography (diameter of column 1.5 cm) on silica gel (Merck, Silica Gel 60) (6-8 g) using hexane-ethyl acetate (9:1) as an eluent.

CHAPTER 5

RESULTS AND DISCUSSIONS

The Suzuki cross-coupling reaction was carried out in the presence of two types of palladium loaded catalysts, which were $\text{Pd}(\text{OAc})_2$ and Pd(II) loaded Y type zeolite. Different aryl halide, base, DMF: H_2O ratio, temperatures and reaction times were employed in order to optimise reaction conditions.

$\text{Pd}(\text{OAc})_2$ solution was prepared to get 1% Pd in zeolite, however by the AAS analysis it was found that Pd content for NaY was 0.68% and for CsY was 0.36%. The Pd amount charged to the reaction medium was 2.5 mol% with respect to arylhalide substrate.

5.1 SUZUKI COUPLING REACTIONS OVER $\text{Pd}(\text{OAc})_2$ LOADED Na-Y TYPE ZEOLITE

5.1.1. Investigation of Suzuki Coupling Reactions with Iodobenzene and 4-Iodoanisole

The activity of $\text{Pd}(\text{OAc})_2$ loaded Y type zeolite catalyst was investigated by using iodobenzene (Avocado, >98%) and phenylboronic acid (Fluka, ≥97%) at the beginning of this thesis study. Iodobenzene and 4-iodoanisole (Merck, >98%) are highly active aryl halides in the formation of C-C bond with phenylboronic acid. C-I bond is the weakest bond among the other C-halide bonds. So, carbon-iodine bond is easily broken and the oxidative addition of palladium to carbon easily occurs. We performed preliminary reactions using phenyl iodide agent.

Table 5.1. The Suzuki reactions of iodoarenes with phenylboronic acid over Pd(OAc)₂-NaY Zeolite

Reactant	DMF:H ₂ O	Time(h)	Yield %
^a Iodobenzene	4:1	5	80-90 %
^b 4-Iodoanisole	8:2	1.5	90 %
^c 4-Iodoanisole	8:2	1.5	0 %
^b 4-Iodoanisole	1:0	1.5	37 %
^b 4-Iodoanisole	1:1	0.5 h	100 %

a: 1 Reaction conditions: 1 mmol iodobenzene, 1.1 mmol phenylboronic acid, 2 mmol K₂CO₃, (5 % Pd) Pd-NaY, DMF/H₂O, at 80 °C under Argon atmosphere.

b: Reaction conditions: 1 mmol 4-iodoanisole, 1.2 mmol phenylboronic acid, 2 mmol K₂CO₃, (2.5 % Pd) Pd-NaY

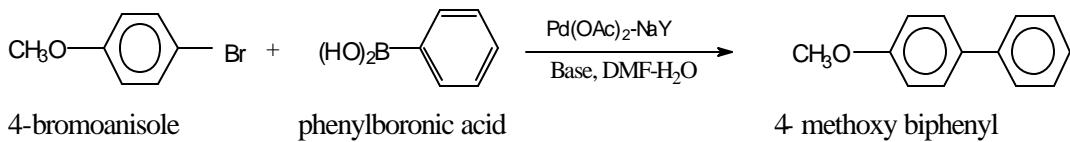
c: K₂CO₃ was not used.

On the basis of the preliminary results given in Table 5.1. following conclusions were considered:

1. Base is an important factor for the Suzuki coupling reactions
2. Different DMF:H₂O ratio influences the reaction yield. Water is a critical factor for the reaction.

5.1.2. Investigation of the Suzuki Coupling Reactions with 4-Bromoanisole

Optimum conditions, DMF: H₂O ratio, temperature, time, and base effects were also investigated for the reaction of 4-bromoanisole (Merck, >98%) with phenylboronic acid in Suzuki coupling reactions in this part.



Scheme 5.1. The Suzuki coupling reaction of 4-bromoanisole with phenylboronic acid.

5.1.2.1. DMF: H₂O Ratio Effect

In this part of study, we wanted to find out an appropriate solvent system that strongly favours the Suzuki coupling of 4-bromoanisole with phenylboronic acid. When 1:1 ratio was used the yield was obtained quantitatively as shown in Table 5.2.

Table 5.2. The effect of DMF:H₂O ratio on the Suzuki coupling reactions of 4-bromoanisole with phenylboronic acid

DMF:H ₂ O	Yield %
1:4	10-20 %
1:2	50-60 %
1:1	100 %

Reaction conditions: 1 mmol 4-bromoanisole, 1.2 mmol phenylboronic acid, 2 mmol K₂CO₃, 0.025 mmol Pd(OAc)₂-NaY (2.5% Pd), total volume was 10 mL, 80 °C, 1.5 h under Argon atmosphere.

5.1.2.2. Temperature and Time Effect

Quantitative yields were obtained at the reaction temperatures of 80 °C and 50 °C. Higher than 96% yield could be obtained at room temperature after 3 h with 4-bromoanisole and phenylboronic acid.

Table 5.3. The effect of temperature and reaction time on the Suzuki coupling reactions of 4-bromoanisole with phenylboronic acid

Time	Temperature	Yield %
1.5 h	80 °C	100 %
1 h	50 °C	100%
1 h	Room temperature	78 %
3 h	Room temperature	96%

Reaction conditions: 1 mmol 4-bromoanisole, 1.2 mmol phenylboronic acid, 2 mmol K₂CO₃, 0.025 mmol Pd(OAc)₂-NaY (2.5% Pd), DMF: H₂O 1, total volume is 10 mL.

5.1.2.3. Effect of Amount and Type of Base

Two types of bases and two different amounts of K_2CO_3 (Merck, 99,5%) were used in this part. When K_2CO_3 amount was increased to 4 mmol from 2mmol, reaction yield increased from 78% to 96 %. The slightly less coupling product < 90% formed when Na_2CO_3 (Carlo Erba 99,5%) was used instead of K_2CO_3 .

Table 5.4. The effect of base type and amount on the Suzuki coupling reactions of 4-bromoanisole with phenylboronic acid

Base	Time	Yield %
^b K_2CO_3	1 h	78 %
K_2CO_3	1 h	96 %
K_2CO_3	15 min	95 %
Na_2CO_3	15 min	90 %

Reaction conditions: 1 mmol 4-bromoanisole, 1.2 mmol phenylboronic acid, 4 mmol K_2CO_3 and Na_2CO_3 $Pd(OAc)_2-NaY$ (2.5% Pd), DMF: H_2O 1, total volume was 10 mL, under Argon , at room temperature.

^b 2 mmol K_2CO_3 was used

5.2. SUZUKI COUPLING REACTIONS OVER $Pd(OAc)_2$ LOADED CsY TYPE ZEOLITE

1mmol 4-bromoanisole and 1.2 mmol phenylboronic acid were reacted in the presence of Cs^+ exchanged Y type zeolite containing Pd (Table 5.5). The reaction medium contained 2.5% Pd with respect to aryl halide and this reaction was carried out under argon atmosphere at 50 °C for 1 h with or without K_2CO_3 .

Table 5.5. Suzuki Coupling reaction with $Pd(OAc)_2$ loaded Cs^+Y

Base	Yield % ^a
-	1.4 %
K_2CO_3	47 %

^a Reaction conditions: 2mmol K_2CO_3 , DMF: H_2O 1, at 50 °C over 1 h.

When Cs^+ cation exchanged to NH_4Y instead of Na^+ cation, 4-methoxybiphenyl yield decreased from 100% to 47% for the same reaction conditions (Table 5.3.). However we expected that Pd(OAc)_2 loaded CsY type zeolite would give higher yield than Pd(OAc)_2 loaded NaY type zeolite because of the higher basicity of the Cs-Y . In contrast to our expectation, Cs^+ loaded Y type zeolite showed poor activity although K_2CO_3 was added. Larger radius of Cs^+ cation might have hindered the reach of reactants to the palladium metal, which is in the zeolite cage.

5.3. REUSEABILITY OF THE Pd(OAc)_2 TYPE ZEOLITE

A salient advantage of heterogeneous catalysts is the ease with which they are separated from the reaction products. Separated heterogeneous catalyst should able to be reused in reactions.

So in this thesis study; the used Pd(OAc)_2 loaded zeolite was used under the same reaction conditions as for the initial run of the catalyst. Pd(OAc)_2 loaded Y type zeolite that was used for the first run (reaction condition: 1 mmol bromoanisole, 1.2 mmol phenylboronic acid, 4 mmol Na_2CO_3 and 1/1 DMF/ H_2O solvent ratio for 15 min at room temperature). Then the catalyst was filtered at the end of the reaction washed with dichloromethane and water and finally dried. The dried catalyst was used under the same reaction conditions without any regeneration. Unfortunately, at the end of this reaction the product yield decreased from 90 % to 6 %.

Although reusability property is so important parameter for heterogeneous catalyst system, this property was not satisfactory for the Pd(OAc)_2 loaded Y type zeolite.

5.4. SUZUKI COUPLING REACTIONS OVER Pd(II) LOADED Y TYPE ZEOLITE

Pd(II)Y catalyst was prepared as mentioned in the Chapter 4. Pd(II) loaded Y type zeolite was analysed by AAS and the amount of palladium in the zeolite was found to be $1\% \pm 0.1$.

Variation of reaction conditions on the Suzuki reaction was examined over the cross coupling of 4-bromoanisole with phenylboronic acid. The cross coupling reaction of 4-bromoanisole and phenylboronic acid was carried out in various DMF:H₂O ratios and base types to optimise the reaction conditions.

5.3.1. DMF: H₂O Ratio Effect

The optimum DMF:H₂O ratio was determined to be 1, as can be seen in Table 5.6. The higher or lower DMF:H₂O ratios lowered the yield. This may be related with the solubility of the reactants and base.

Table 5.6. The effect of DMF:H₂O ratio on the Suzuki coupling reactions of 4-bromoanisole with phenylboronic acid

DMF:H ₂ O	Yield ^b %
1/1	93 (92)
2/1	65
1/2	77

^a Reaction conditions: 1.0 mmol of 4-bromoanisole, 1.2 mmol of phenylboronic acid, 4 mmol Na₂CO₃, 0.025 mmol Pd, of total volume was 10 mL, 1 h at room temperature.

^b GC yields based on 4-bromoanisole. The isolated yields are in parenthesis.

5.3.2. Base Type and Amount Effect

Base type and amount are so important parameter for Suzuki coupling reactions as shown in Table 5.7.

Table 5.7. The effect of the base type and the amount on the Suzuki coupling reactions of 4-bromoanisole with phenylboronic acid

Base	Yield% ^b
Na ₂ CO ₃ (3 mmol)	81
Na ₂ CO ₃ (4mmol)	93
Na ₂ CO ₃ (5mmol)	77
K ₂ CO ₃ (4mmol)	> 99
CsCO ₃ (4mmol)	68
Li ₂ CO ₃ (4mmol)	63
Cs ₂ CO ₃ (4mmol)	70
NaOAc (4mmol)	3
N(C ₂ H ₅) ₃ (4mmol)	3
NaOH (4mmol)	7

^a Reaction conditions: 1.0 mmol of 4-bromoanisole, 1.2 mmol of phenylboronic acid, 0.025 mmol Pd, DMF:H₂O 1, total volume was 10 mL, 1 h at room temperature under argon.

^b by GC

The results given in Table 5.7 could be summarized as follows

1. When 4 mmol Na₂CO₃ was used the reaction yield was the highest (amount of base).
2. The coupling product formation was quantitative in the presence of K₂CO₃. The reason might be that, basicity of K₂CO₃ cation is higher than Na₂CO₃ cation. So this might influence the mechanism of Suzuki coupling reaction. CO₃²⁻ anion that belongs to K₂CO₃, might easily be inserted to the palladium metal because of larger radius of K⁺.
3. The coupling product formations were moderate with Li₂CO₃ and Cs₂CO₃. Although, in literatures, the highest product yield, in general was obtained in the presence of Cs₂CO₃, in our reaction the highest product yield was obtained when K₂CO₃ was used. The reason might be that Cs⁺ has a higher radius and this property influences diffusibility of reactants toward the active palladium species.
4. The catalyst showed very poor activity in the presence of N(C₂H₅)₃, NaOH or NaOAc as bases (<8%).

5.3.3. Halogen and Substituent Group Effects

Catalyst testing was performed also on a variety of aryl halides (Table 5.8). 4-Bromonitrobenzene afforded only a moderate yield of the corresponding coupled product though it is an activated aryl bromide, while phenyl bromide and other activated aryl bromides afforded excellent product formation under the established conditions. 4-Iodoanisole was converted to the corresponding coupled product quantitatively. A moderate yield was obtained with an activated chloroarene, 4-chlorobenzotrifluoride (52% by GC) when the reaction was performed at 100 °C. Nevertheless the conversion of the activated chloroarene was complete and the fate of the remaining starting material is unknown as no dehalogenated or any other side products could be determined by GC analysis.

Table 5.8. The effect of halogens and substituent groups on the Suzuki coupling reactions of 4-bromoanisole with phenylboronic acid.

Aryl halide	Arylboronic Acid	Yield % ^b
4-NO ₂ C ₆ H ₄ Br	C ₆ H ₅ B(OH) ₂	54(44)
C ₆ H ₅ Br	4-MeC ₆ H ₄ B(OH) ₂	(94)
4-CNC ₆ H ₄ Br	C ₆ H ₅ B(OH) ₂	90 (64, 78 ^c)
4-MeCOC ₆ H ₄ Br	C ₆ H ₅ B(OH) ₂	>99 (88)
4-MeOC ₆ H ₄ I	C ₆ H ₅ B(OH) ₂	>99
4-CF ₃ C ₆ H ₄ Cl	C ₆ H ₅ B(OH) ₂	52 ^d

Reaction conditions: 1.0 mmol of 4-bromoanisole, 1.2 mmol of phenylboronic acid, 0.025 mmol Pd, DMF:H₂O 1, total volume was 10 mL, 1 h at room temperature.

^b GC yields based on 4-bromoanisole. The isolated yields are in parenthesis.

^c recrystallize with hexane

^d at 100°C

5.3.4. Time and Temperature Effect

The reaction of 4-bromoanisole with phenylboronic acid was also conducted at 0.5 and 1.5 h reaction times in the presence of Na₂CO₃ under the established reaction conditions. In both cases the yield was identical to that obtained at 1 h. This could be associated with the deactivation of the palladium catalyst, as the formation of coupled

product ceased in the first 0.5 h of the reaction and aryl bromide conversion was incomplete.

Table 5.9. The effect of temperature and reaction time on the Suzuki coupling reactions of 4-bromoanisole with phenylboronic acid

Time	Yield %
30 min	97
1 hour	93
1.5 hour	93
1 hour ^b	100

Reaction conditions: 1.0 mmol of 4-bromoanisole, 1.2 mmol of phenylboronic acid, 0.025 mmol Pd, 4 mmol Na₂CO₃, DMF:H₂O 1, total volume was 10 mL, at room temperature under argon.

b: at 50⁰C.

5.3.5. Ligand Effect

4-Bromoanisole and phenylboronic acid were reacted with Pd(II) loaded Y type zeolite in the presence of ligands which were dimethylphenylphosphine and 3-methylbenzothiazolium iodide for 1 hour at room temperature. Phosphines are used in many Pd catalysed reactions. Benzothiazolium salts were also found to activate palladium as a ligand [47]. These ligands were used in an amount 2 fold molar equivalent with respect to the Pd amount. First of all ligands were added into the reaction flask with catalyst (to obtain Palladium-ligand complex) in the presence of 2 mL DMF as a solvent and the mixture was stirred for 15 min. Then all reactants and the rest of the solvent (3 mL DMF, 5mL water) were added into the reaction flask and this reaction was continued 1 hour more. However, in our case, the addition of PPh(CH₃)₂ or 3-methylbenzothiazolium iodide which possess suitable molecular sizes to be able to penetrate through the zeolite apertures (~7 Å), brought the coupling reaction to a halt.

5.5. REUSEABILITY OF THE Pd(II)Y TYPE ZEOLITE

Pd(II) loaded Y type zeolite was used in a Suzuki coupling under the following conditions: 1 mmol bromoanisole, 1.2 mmol phenylboronic acid, 4 mmol Na₂CO₃ and 1/1 DMF/H₂O solvent ratio at room temperature for 1 hour. The catalyst was filtrated and washed with dichloromethane and water at the end of this reaction (Table 5.10.). The dried catalyst could not be reused at the same reaction condition without activating it. We determined that the used catalyst recovers its activity when it is re-calcinated under O₂ by using the same method applied for the preparation of the fresh catalyst precursor. It was evident that the first regeneration process increased the catalyst activity, as the yield was quantitative at the 2nd use of the catalyst. However, there was little decrease in activity at the 3rd, affording 90% yield, and the coupling formation was reduced to 62% at the 4th use of the catalyst at room temperature. But, the catalyst showed again high activity at the 4th use when the reaction was carried out at 50°C, in this case the product formation being quantitative.

Table 5.10. Reaction of 4-bromoanisole with phenylboronic acid using recovered and regenerated Pd(II)-NaY as catalyst

Catalyst cycle	Yield% ^b
First	93
Second	>99
Third	90
Fourth	62
Fourth ^c	>99

^aReaction conditions are same as those of entry 1 in Table 1.

^bGC yields based on 4-bromoanisole.

^c at 50°C.

5.6. LEACHING TEST

The leaching of active species from heterogeneous catalysts used in solution is a crucial question in order to identify whether the active centres are immobilized in the zeolite framework or dissolved palladium complexes in the homogeneous solution. The leaching was studied as follows: The reaction mixture, in which 1 mmol 4-bromoanisole

and 1.2 mmol phenylboronic acid was reacted in the presence of 4 mmol Na₂CO₃ and 1:1 DMF:H₂O at room temperature over 1 hour (over the Pd(II) loaded NaY type zeolite) in the presence of 0.025 mmol Pd, was separated from catalyst. All of the solvent was evaporated and residue was digested with H₂O₂ and HNO₃ and then diluted with ultra pure water. Afterwards, Pd in the diluted solution was determined by AAS so as to check whether Pd leaches during the reaction. Pd concentration was found to be 1.35 ppm. 1.35 ppm Pd(OAc)₂ (instead of Pd(II)) was reacted with 1 mmol bromoanisole, 1.2 mmol phenylboronic acid and 4 mmol Na₂CO₃, at room temperature for 30 minute to investigate whether this amount of Pd(OAc)₂ catalyses our reaction or not. The yield was found 3% at the end of this reaction in homogeneous system. However when this reaction was carried out with Pd(II) loaded NaY type zeolite at this reaction conditions the yield was found to be 97% (Table 5.9.), and with 0.025 mmol of Pd(OAc)₂ the product formation was quantitative. This may indicate that the leaching of Pd cannot explain the overall activity of the catalyst.

5.7. RESULTS OF UV ABSORPTION OF PALLADIUM LOADED Y TYPE ZEOLITE

The presence of the Pd(NH₃)₄²⁺ cations in the zeolite is confirmed by an absorption at approximately 299 nm, which agrees well with earlier literature data as seen in the Figure 5.1. [48]. This UV spectrum shows us that Pd(NH₃)₄²⁺ loaded zeolite didn't contain the same form of palladium after being calcinated under O₂.

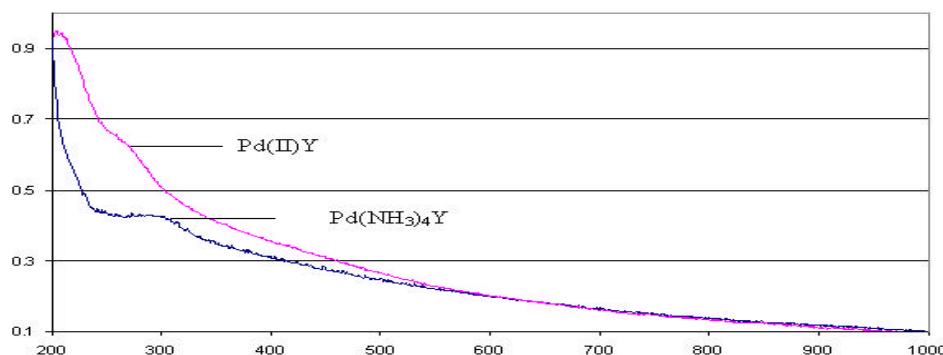


Figure 5.1. UV absorption of Pd(II) and Pd(NH₃)₄²⁺ loaded Y type zeolite

5.8. X-RAY DIFFRACTION ANALYSIS OF Pd(II) LOADED Y TYPE ZEOLITE

The nature of the Pd(II) species were obtained by calcination of $\text{Pd}(\text{NH}_3)_4^{2+}$ -Y under O_2 . The 1 wt % Pd-Y, turns into pink upon calcinations (as it was indicated in literature) after this calcination it contains Pd^{2+} cations. But the colour of the Pd(II) loaded Y type zeolite, which was used and regenerated for second usage was slightly tobacco colour. This tobacco colour may indicate that PdO clusture could be formed on the external surface of the Y type zeolite [48]. To investigate this phenomenon, X-ray analyses of Pd(II) Y type zeolite and second used Pd(II) Y type zeolite were done. As seen in the below diffractogram there are no differences in the crystal structure of NaY, Pd(II)-NaY and second used Pd(II)-NaY zeolite and no information could be gained regarding the natural Pd (from diffractograms) as they are dominated by X-ray patterns of the zeolite (Figure 5.2.).

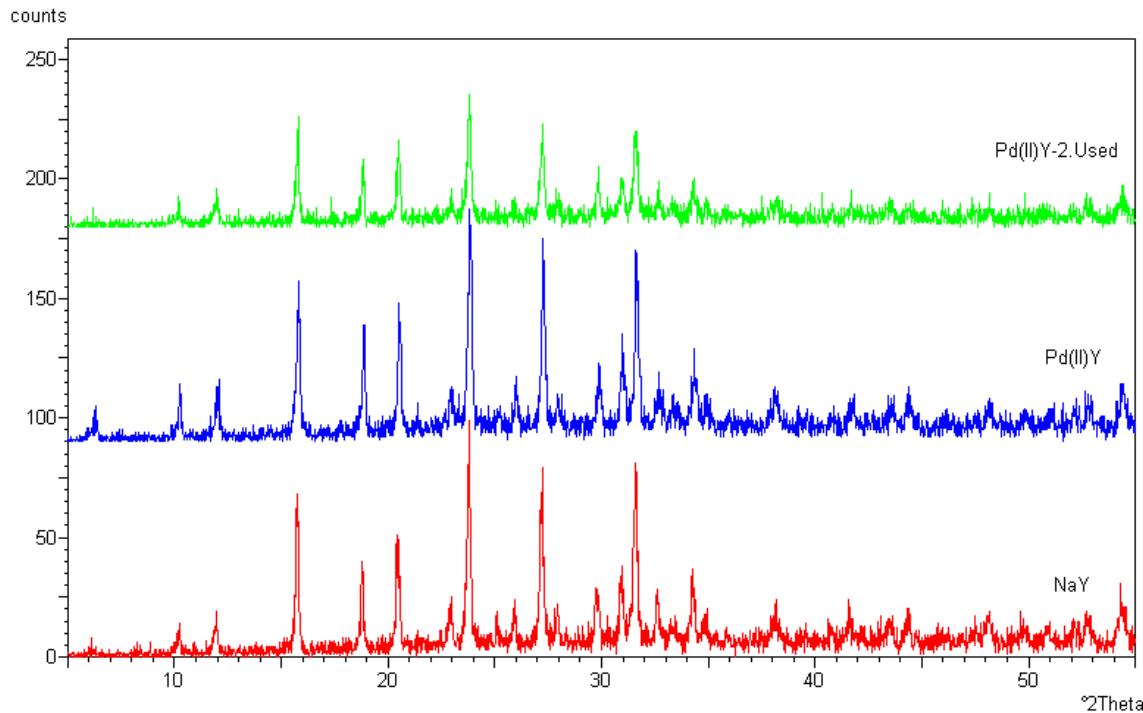


Figure 5.2. X-Ray Diffractogram of NaY, Pd(II)Y and second used Pd(II)Y

CHAPTER 6

CONCLUSION

In this thesis study; two different types of palladium complexes were loaded in the Y type zeolite, which were $\text{Pd}(\text{OAc})_2$ and $\text{Pd}(\text{NH}_3)_4^{2+}$. Unfortunately, the reusability of the $\text{Pd}(\text{OAc})_2$ loaded Y type catalyst was not satisfactory to be an appropriate heterogeneous catalyst for the Suzuki coupling reactions although this property is so important parameter for heterogeneous catalyst systems. In contrast to $\text{Pd}(\text{OAc})_2$ loaded Y type zeolite, Pd(II) loaded Y type zeolite, which was prepared from $\text{Pd}(\text{NH}_3)_4^{2+}$ loaded Y type zeolite, could be reused subsequent to regeneration.

It was found that base type and amount played a critical role in the Suzuki coupling reaction. DMF: H_2O ratio was found to be another important parameter that influenced the reaction. The highest yield was obtained when DMF: H_2O ratio was 1:1.

On the basis of the mentioned results, it can be stated that in homogeneous chemistry, the choice of the ligand plays a critical role in the Suzuki cross-coupling reactions of aryl halides. On the contrary, the Pd(II)Y catalysts activate aryl bromide toward the Suzuki coupling reactions under mild conditions without adding ligand. We found that added ligands were deleterious to the Pd(II)Y catalysed reaction. The reason of this may be that these ligands prevent the reach of the reactants to the Pd(II), which is in the cage of the Y type zeolite.

When the leaching of Pd(II) from Pd(II) loaded zeolite was investigated, 1.35 ppm Pd was detected at the end of reaction. Only 3% yield was provided by 1.35 ppm palladium containing $\text{Pd}(\text{OAc})_2$. However when this reaction was taken place at this reaction conditions with Pd(II) loaded NaY type zeolite the yield was found 97%. So we can say that our reaction took place in heterogeneous system.

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