Benzylation of Benzene Over Rare Earth Exchanged Zirconium Pillared Montmorillonite

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Abstract:*In this present work, zirconium pillared montmorillonite and rare earth exchanged zirconium pillared montmorillonite were prepared and their catalytic performance was studied for the Friedel –Crafts Benzylation reaction. The rare earths selected are Lanthanum (La), Cerium(Ce) and Samarium(Sm). The physicochemical characterization was performed using X-ray diffraction(XRD), BET surface area measurement(BET-SA) and scanning electron microscopy(SEM). The surface acidity of the prepared systems was studied by stepwise temperature programmed desorption (TPD) of ammonia. The catalytic activity of the prepared systems was studied by selecting Friedel-Crafts alkylation reaction of benzene with benzyl chloride. Enhancement of surface area, acidity and shift of XRD peak towards lower 2θ region suggest efficient pillaring. Zirconium pillared clays at room temperature was found to be very effective catalysts for the catalytic benzylation of benzene with benzyl chloride. Among the various rare earth exchanged forms, the Sm exchanged Zr pillared montmorillonite shows the highest activity and the least activity is shown by Ce exchanged one.*
Keywords: *Friedel-Crafts Benzylation, Pillared clays, rare earths, zirconium pillared montmorillonite,*

I. Introduction

Friedel- Crafts reaction has become an indispensable tool of organic chemistry, covering wide range of reactants. Alkyl aromatics produced by these reactions are the precursors of various industrially important compounds. Strongly acidic catalysts are required for the efficient catalysis of Friedel –Crafts reactions. Among the Lewis acids, anhydrous aluminium chloride was the most widely employed reagent to trigger the Friedel-Crafts reaction **[1]**. The major disadvantages encountered in the use of anhydrous aluminium chloride include corrosion, difficulty in the separation and recovery, disposal of spent catalyst, high toxicity etc. In light of these factors, there was a long felt need and demand to substitute these reagents by reusable environment friendly solid acid catalysts n the Friedel –Crafts reactions. Intensive research in this direction revealed the materials in the form of solid acids developed from natural clay, zeolites, sulfated zirconia, pillared clays etc [2, 3].

Pillared interlayered clays (PILCs) find many applications in the field of catalysis. Earlier works reported that pillared clays showed a significant modification effect in its porous structure and physicochemical properties [4]. Currently montmorillonite (M) clay is considered to be a most probable material in various catalysis reactions. A number of different cations, such as aluminium[5], titanium[6] , iron[7], chromium[8] and zirconium[9,10]   polycations have been used for the preparation of pillared M. The basic phenomenon used in the preparation of pillared clays is the ion exchange of interlamellar cations by the bulky cationic species (oligomer) that act as probes to keep the structure open. It is obvious that only the swelling clay minerals capable of cation exchange can be pillared [11]. To get a stable structure such as pillared clay, the intercalated solid has to be carefully processed further. Treatment of the solid at an elevated temperature is the next step after intercalation. This results in the dehydration and dehydroxylation of the polycation where it changes to stable oxide. Upon calcinations, the bond between the interlayer species and clay layers is thought to shift from ionic to near covalent, which results in the stabilization of the porous network by converting hydroxide pillars to stable oxides [12,13]. N. Ahmad et.al reported that cobalt nanoparticles supported on Zr-PILC acts as powerfull catalyst for Fischer-Trop's reaction [12]. Choudhary et al. have been preparedCyclopentyl and cyclohexyl derivatives of benzene, toluene, o and p-xylene, mesitylene and anisole in 85–95% yield by refluxing a solution of the respective aromatic substrate with cyclopentanol or cyclohexanol in 1,2-dichloroethane on Fe^{3+}-montmorillonite with 10 mol% of TsOH or MsOH as cocatalyst[14].

Choudhary et al.have benzylated anisole, mesitylene, p-xylene, toluene and naphthalene with high degree of conversions, using benzyl choride. They observed that calcing increases the activity of the catalyst, and that the higher the calcing temperature the more active the catalyst is. They attribute this to dehydration at 200 °C, formation of metal oxides on calcing at 500 °C and higher temperatures up to 800 °C. They also found that the used catalyst is more active than the one used for the initial reaction. This observation is explained as

due to a possible formation of Lewis acid sites resulting from the reaction of HCl liberated in the benzylation process [15].

The present study evaluates the effectiveness of zirconium pillared montmorillonite and rare earth exchanged zirconium pillared montmorillonite for the Friedel-Crafts benzylation of benzene with benzyl chloride. The physicochemical characterization was performed using X-ray diffraction(XRD), BET surface area measurement(BET-SA) and scanning electron microscopy(SEM).The surface acidity of the prepared systems was studied by stepwise temperature programmed desorption (TPD) of ammonia. The effect of different reaction variables like molar ratio of the reactants, amount of catalyst, temperature, time, total volume of the reactants and moisture sensitivity of the catalyst were also studied.

II.   Experimental

We have synthesized Zirconium pillared Montmorillonite and rare earth metals (eg. La, Ce and Sm) exchanged Zirconium pillared montmorillonites.

2.1. Preparation of Zirconium pillared montmorillonites.

Zirconyl nitrate solution (0.1M) was prepared and aged for 24h. 2% suspension of parent montmorillonite was also prepared by stirring with deionised water for 5 h and kept overnight. The pillaring solution, after ageing was then added drop wise to the clay suspension with stirring after adjusting the pH to 1.9. Final solution was stirred for 24 hours at room temperature. It was then aged for 4 days, washed free of nitrate, dried at 120°C for 12 hours and calcined at 350°C for 12 hours. The pillared montmorillonite at high temperature was prepared by adding the pillaring solution at a temperature of 70° C and the final solution was then stirred for 2h at this temperature for uniform pillaring.   After this it was stirred for 24h at room temperature.

2.2. Preparation of rare earth exchanged Zr pillared Montmorillonite

For the preparation of rare earth exchanged Zirconium pillared montmorillonite a 2% suspension of parent montmorillonite was prepared by stirring with 500 ml 0.1 M rare earth salt solution for 8h. After decantation another 500ml solution was added and stirred for 8h. This process was continued until the total stirring time was 24 hours. It was then kept for overnight and the pillaring was carried out by adopting the above procedure.

2.3 Notations of Catalysts

M	Parent montmorillonite
ZM$_R$	Zirconium pillared montmorillonite at room temperature
ZM$_H$	Zirconium pillared montmorillonite at high temperature
LZM$_R$	Lanthanum exchanged Zirconium pillared montmorillonite at room temperature
CZM$_R$	Cerium exchanged Zirconium pillared montmorillonite at room temperature
SZM$_R$	Samarium exchanged Zirconium pillared montmorillonite at room temperature
SZM$_H$	Samarium exchanged Zirconium pillared montmorillonite at high temperature.

2.4 Characterization Techniques

X-ray diffraction is one of the most widely used techniques in the field of heterogeneous catalysis. It can provide information about the three dimensional structure of the solid substance, their composition and crystallinity. Transition to different phases, allotropic transformation and purity of the substance can also be identified by this technique. The mean crystallite size of the substance can also be determined from the broadening of an X- ray diffraction peak.The XRD patterns of the entire sample were obtained using RIGAKU D/MAX-C instrument within a 2θ range of 2° to 10° and a rotation of 2° /min.

The surface area of all the catalysts was determined by BET nitrogen adsorption at liquid nitrogen temperature using a Micromeritics Flow Prep-060 instrument. Previously activated samples were preheated and degassed at 200°C for 2hrs under nitrogen flow. The catalyst is then brought to 77K using liquid nitrogen for adsorbing nitrogen gas at various pressures. The total pore volumes of the samples were also measured using the instrument.

SEM is used to study the topography as well as the crystalline nature of the catalyst samples. The instrument used in the present study is JEOL GSM- 840A Oxford England Model with resolution 1.38eV.

Temperature programmed desorption (TPD) is one of the basic experimental tools of surface science for the identification of desorbing species, to find out the acidity and acid strength distributions and for obtaining their desorption kinetics. The acid contents were established from the amount of ammonia adsorbed at 300°C, followed by temperature programmed desorption at 400°C.

2.5. Catalytic activity Measurement

2.5.1   Liquid Phase Friedel – Craft`s Alkylation

The liquid phase catalytic reaction performed was benzylation of benzene. All the liquid phase reactions were carried out in a 50ml round-bottomed flask equipped with an oil bath, a magnetic stirrer and a reflux condenser.

For the benzylation of benzene 0.1g of the activated catalyst was kept in the round- bottomed flask after mixing the alkylating agent and the substrate in the desired molar ratio and was allowed to attain the reaction temperature. After the reaction time, the catalyst was separated from the reaction medium and the products were analyzed using a gas chromatograph Chemito GC 8610 fitted with an SE 30 column and a flame ionization detector. The effect of various parameters like temperature, reactant molar ratio, time, reactant volume, amount of catalysts, moisture adsorption etc. were studied.

III.   Results & Discussion

3.1 Inference from Characterization Studies

Table 3.1.   Surface area, d_{001} spacing and acidity of the various catalyst systems.

Catalyst	Surface area (m^2/g)	d_{001} spacing (A^o)	Acidity $(mmol/g)$
M	39.24	9.82	0.0161
ZM_R	201	21.53	1.2080
ZM_H	104	19.61	1.6962
LZM_R	155	15.09	1.2757
CZM_R	157	14.35	0.7688
SZM_R	212	24.52	1.4091
SZM_H	109	15.91	1.3213

The characteristic d_{001} spacing of the parent montmorillonite (M) is obtained at a 2θ value of 9.00 corresponding to 9.82 A^o[16].   The increase in d_{001} spacing shows the expansion of the clay layer during the zirconium pillaring. The shift in 2θ values to lower region is shown in Fig. 3.1.
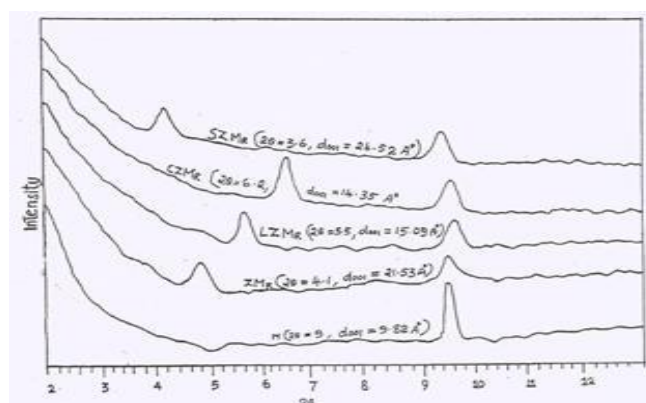

Figure 3.1 XRD patterns of zirconium pillared and rare earth exchanged zirconium pillared   montmorillonite.

Even in case of Sm exchanged catalysts, room temperature pillaring is more efficient as can be seen from the surface area and d-spacing results. A comparison of the rare earth exchanged Zr pillared montmorillonites shows that Sm pillaring is most effective as it gives the maximum surface area & d- spacing.

Due to the rare earth exchange and zirconium pillaring the surface area and acidity of the various catalyst systems were increased. Bineesh et al. reported similar results [17]. The larger surface area is ascribed to the result of increased pore volume and formation of new pores because of Zr-pillaring. These results can be well correlated with the catalytic activity measurement.

We have found that room temperature is best suited for Zr pillaring of montmorillonite. In case of ZM_R and ZM_H we find that there is a drastic difference between surface area and d- spacing values indicating that efficient pillaring has not occurred. The SEM photograph of ZM_H shown in fig.3.2. clearly points out that agglomerization of particles has taken place leading to a reduced surface area.

Figure 3.2. SEM photograph of ZM_H showing agglomerization

3.2 Catalytic Activity of Zirconium Pillared Clays In Liquid Phase Friedel- Crafts Alkylation.
3.2.1. Benzylation of Benzene

       Benzylation of benzene has been carried out using benzyl chloride. The function of a catalyst is to provide assistance for a particular chemical reaction by providing an alternate path of lower activation energy. The general scheme of the reaction can be represented as in fig. 3.3. The results obtained show that the reaction is faster and the mono- alkylated product was obtained predominantly with little or no di- alkylated product during this reaction. The optimization process was done by varying the reaction parameters like molar ratio, total volume of reactants, time, temperature and amount of catalyst.
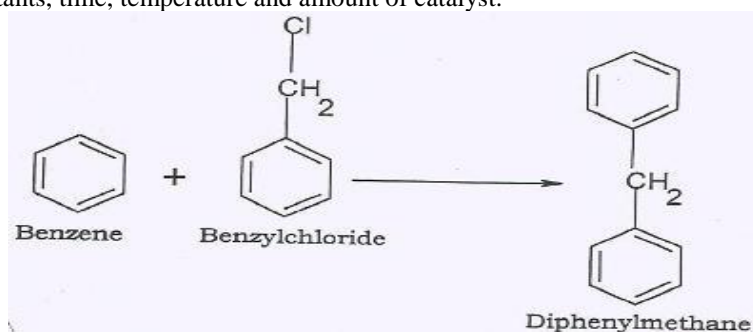

Figure.3.3. General reaction scheme for benzylation of benzene

3.2.2 Effect of Temperature

       To investigate the influence of temperature on the reaction, a number of experiments were carried out at different temperatures keeping other reaction conditions the same. The results are shown in the Fig 3.4.

       The temperature selected for the study was in the range $60^{o}C$ to $100^{o}C$. At a lower temperature, 100% selectivity was obtained but the conversion of benzyl chloride was very low. As the temperature increases the conversion also increases. After $80^{o}C$, there was a sudden increase in conversion and a selectivity of 100% was achieved. A further increase of temperature increases the conversion but the selectivity decreases.
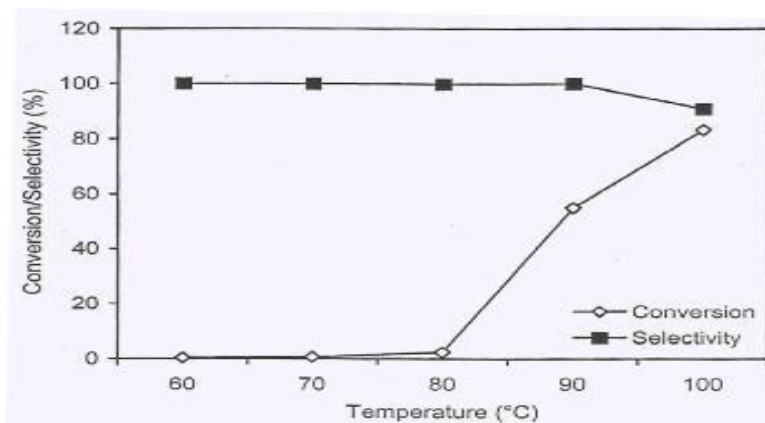
Figure.3.4. Effect of temperature on conversion and product selectivity for the benzylation of benzene.

Reaction condition :- Benzene to benzyl chloride molar ration 10:1, time 1 h, amount of catalyst 0.1g, total volume of reactants 10 ml. SZM_R catalyst.

The boiling point of the benzene- benzyl chloride mixture is approximately 85^oC. The optimum temperature selected for the reaction was 90^oC. At this temperature the boiling point is attained at an optimum rate and most of the reactant molecules acquire sufficient activation energy thereby boosting the conversion. Further increase in temperature resulted an increase in conversion at the expense of selectivity. This is because the increased temperature could provide necessary activation for di- alkylation also.

3.2.3 Effect of Benzene- Benzyl Chloride Molar ratio

The variation in the catalytic activity with benzene to benzyl chloride molar ratio was also examined for SZM_R. The conversion and product selectivity at different molar ratios are illustrated in Fig. 3.5.
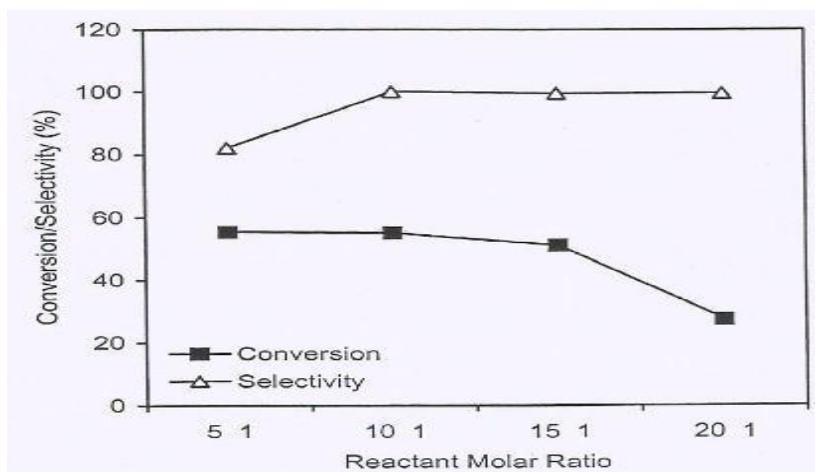

Figure. 3.5 Influence of molar ratio on conversion and selectivity

Reaction conditions :- Temperature 90^oC, amount of catalyst 0.1g, total volume of reactants 10ml, time-1 h. SZM_R catalyst.

The increase in benzene to benzyl chloride molar ratio resulted in lowering of the percentage conversion and selectivity. At low molar ratio the concentration of benzyl cations are very high and this favours the alkylation. At higher benzene to benzyl chloride molar ratios, the concentration of benzyl chloride is very low compared to benzene.

Therefore benzene may get adsorbed over the catalyst surface, suppressing the adsorption of benzyl chloride. Due to the deficiency of benzyl cations the conversion decreases but the selectivity remains almost same. The optimum molar ratio selected for this reaction was 10:1 at which a selectivity of 100% and conversion of 54.97 was obtained.

3.2.4 Effect of total volume of reactants

The dependence of benzyl chloride conversion and product selectivity on the total volume of the reactants is given in Fig. 3.6.
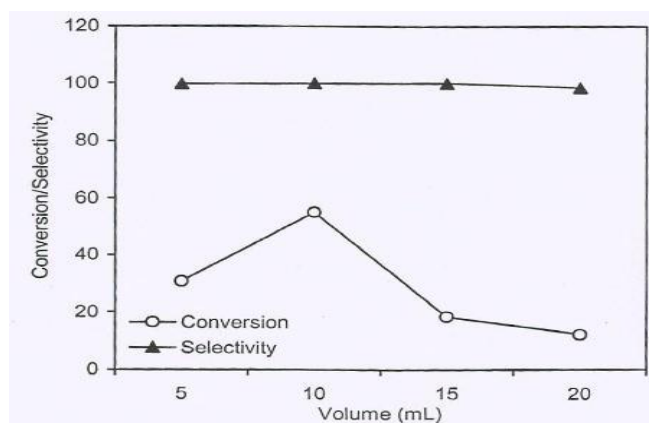
Figure. 3.6. Effect of total volume of reactants on the conversion and selectivity
Reaction conditions :- Temperature 90°C, amount of catalyst 0.1g, benzene to benzyl chloride molar ratio 10:1, time 1h, SZM$_R$ catalyst.

With an increase in the total volume of reactants from 5ml to 20 ml the conversion and selectivity is found to decrease. This is due to the increase in reactant to catalyst ratio. Since the amount of catalyst is fixed at 0.1g, there are no additional surface sites available for adsorption relative to the number of reactant molecules. Therefore the conversion decreases. Initially from 5ml to 10 ml, there is a remarkable increase in conversion.   This may be due to the fact that at very low reactant volumes, the amount of catalyst is too high and hence the product may not be able to diffuse through the catalyst particles efficiently. As the volume increases, the number of reactant molecules also increases thereby escalating the concentration gradient and hence favouring diffusion.

3.2.5 Effect of Time

The progress of reaction monitored with time for the benzylation of benzene with benzyl chloride is portrayed in fig. 3.7.

It is seen that as the time increases from 30 to 120 minutes the conversion increases steadily from 6% to 93%. The reaction will run into completion after 2.5h. But the selectivity values show a decrease with time. This may be due to the fact that the mono- alkylated product undergoes further alkylation that leads to a decreased selectivity for monoalkylated products.
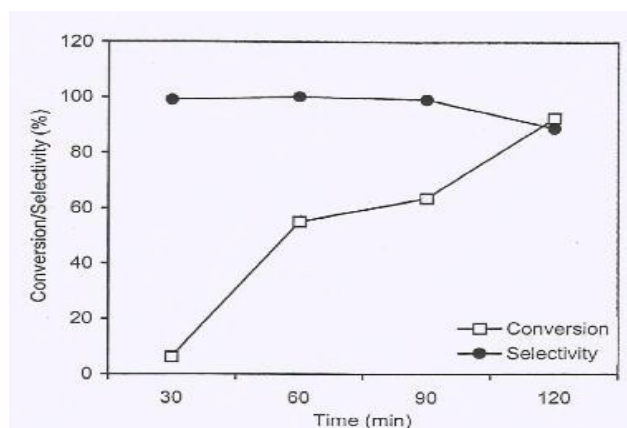

Figure.3.7. Conversion and product selectivity as a function of time.
Reaction conditions:- Temperature 90°C, amount of catalyst 0.1g, benzene to benzyl chloride molar ratio 10:1, total volume of reactants 10mL, SZM$_R$ catalyst.

3.2.6.Effect of Amount of catalyst

The influence of the amount of catalyst on the benzylation of benzene was studied using different catalyst amounts. The conversion of benzyl chloride and selectivity of the product is shown in Fig. 3.8.
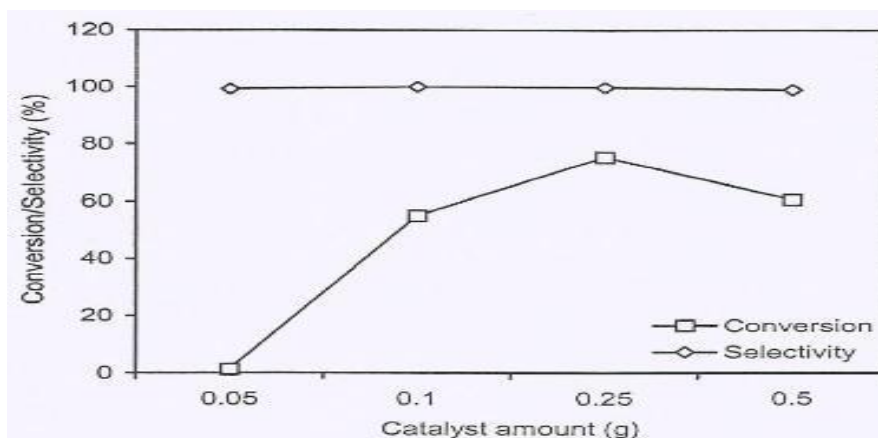
Figure.3.8. Effect of amount of catalyst on benzyl chloride conversion.

Reaction conditions:- Temperature 90°C, benzene to benzyl chloride molar ratio 10:1, total volume of reactants 10mL, time 1 h, SZM_R catalyst.

As the amount of catalyst increased from 0.05g to 0.25g there was a prominent increase in the conversion. This can be explained by taking into consideration the fact that an increase in the amount of catalyst augments the number of surface sites available for adsorption. When more sites are available, more reactants get adsorbed and converted, which is evident from the conversion values. A further increase in the amount of catalyst to 0.5g decreases the conversion. This is because as the amount of catalyst increases beyond a certain limit, diffusion factors come into play.

Since the rate of stirring is kept constant, a resistance to mass transfer occurs and so the reactants are unable to diffuse efficiently through the catalyst particles and pores. The stirring provided is not enough to overcome this mass transfer resistance thus ending up in a poor conversion.

3.3 Effect of Temperature on pillaring

To study the effect of temperature on the pillaring process, the addition of pillaring solution to the clay suspension was carried out at two temperature viz: room temperature and 70°C (high temperature). The results are given in Table 3.3.

Table 3.3 Influence of temperature on Zr pillaring of montmorillonite.

Reaction conditions :- Temperature 90oC, benzene to benzyl chloride molar ration 10:1, amount of catalyst 0.1g, volume of reactants 10mL, time 1h.

Catalyst	Surface Area (m^2/g)	d-Spacing (A^o)	Acidity mmol/g	Conversion (%)
ZM_R	201	21.53	1.208	65.64
ZM_H	104	13.61	1.6962	46.47
SZM_R	212	24.52	1.4091	54.97
SZM_H	109	15.91	1.3213	28.61

The results show that pillaring carried out at room temperature is more efficient as evidenced from the higher values of surface area and d- spacing. Upon samarium exchange before pillaring, the surface area and d- spacing improves whereas the acidity remains almost the same. Samarium being a large cation causes the exchange of pillaring species to be slow thereby producing effective pillars. Even though the acidity of these catalysts was almost same, room temperature pillared catalysts show higher conversion than the high temperature analogue. At high temperature, the pillaring species i.e., the Zr_4 oligomer, may collapse and may get transformed into lower oligomers i.e., Zr_2 species, resulting in non- uniform and inefficient pillaring. This is supported by the decrease in d- spacing and surface area. Hence, based on the surface area and d- spacing values we can conclude that room temperature is best suited for Zr pillaring of montmorillonite.

3.4 Influence of rare earth exchange before pillaring

The effect of rare earth exchange before pillaring in zirconium pillared montmorillonite was studied. The results are tabulated in Table 3.4.

Table 3.4 Influence of rare of earth exchange before pillaring on the Zr pillaring of montmorillonite Reaction conditions:- Temperature 90°C, benzene to benzyl chloride molar ratio 10:1, amount of catalyst 0.1g, volume of reactants 10ml, time 1h.

Catalyst	Conversion	selectivity
ZM_R	65.47	100
LZM_R	29.92	99.01
CZM_R	13.00	98.98
SZM_R	54.97	100

From the results we can see that the ZM_R catalyst possesses maximum activity. In the case of ZM_R, zirconium pillaring species are almost invariably assumed to be based on Zr_4. The ageing of pillaring solution for 24h helps to develop random polymers in solution. In the case of ZM_R the d- spacing obtained is 21.53 A°. This shows effective pillaring at room temperature. The acidity is improved by a large amount as a result of the creation of new active surface sites. In the preparation of rare earth exchanged Zr pillared montmorillonite, the Na^+, Ca^{2+}, and K^+ ions originally present in the interlamellar space with no fixed sites were replaced with hydrated rare earth ions. Addition of these rare earth materials improved the thermal stability of zirconium pillared clays. The exchange of rare earth ions before pillaring makes the pillaring process very slow. Hence the incorporation of the Zr polycation should take place with increased efficiency. In this case, except for Sm exchanged system, other systems show a decreased value for d- spacing as well as surface area. This may be due to the fact that since the pillaring process is slowed down because of the presence of a bulkier rare earth ion instead of smaller alkaline or alkaline earth ion, more time may be required for the complete exchange of these by the bulkier Zr polycation. Here we have provided 24h stirring which may not be sufficient for the rare earth exchanged systems.

CZM_R shows a decrease in conversion for benzylation of benzene even though it has moderate surface area and d- spacing. The surface area and d- spacing of this catalyst were 157.43 m^2/g and 14.35A° respectively. The lowering of conversion may be due to the effect of cerium. The hydrated cerium ions present in the CZM_R catalyst are converted to CeO_2 on calcinations. CeO_2 is well known for its highly basic nature. Due to this reduces the acidity of the clay mineral to a considerable extent, which is clear from the acidity values depicted in Table 3.1. Benzylation of benzene requires a moderate acidity which is not provided by the Ce exchanged system leading to a lower conversion.

SZM_R has emerged as an excellent catalyst in terms of its surface area and d- spacing values. Here we find that the Sm exchange has made the pillaring process slow and the Zr polycation exchange takes place more efficiently. But the intensity of exchange is only about 45%. This proves that more time should be provided during the pillaring process.

The acidity values of the various catalyst systems are almost constant except CZM_R. The high acidity may be due to the effect of metal leaching. We had prepared all the catalyst systems after adjusting the pH to 1.9 by adding a HCl-KCl buffer. Treatment of the clay with HCl results in the removal of octahedral Al^{3+} from the clay layers thereby increasing the Si/Al ratio and hence the total acidity of the system.

In general the study of the benzylation of benzene by benzyl chloride on various pillared clays has shown that under the optimized conditions, the zirconium pillared montmorillonite at room temperature (ZM_R) works as an efficient catalyst. The rare earth exchange in these zirconium pillared clays lowers the catalytic activity. Out of the various rare earths Sm exchanged zirconium pillared montmorillonite shows maximum catalytic activity.

IV. Conclusion

Pillaring of montmorillonite with polyoxocations of Zirconium resulted in the satisfactory incorporation of metals into the clay layers. The incorporation of zirconium and rare earth metals like La, Ce and Sm affects the physic-chemical characteristics of the parent montmorillonite. Enhancement of surface area, acidity and shift of XRD peak towards lower 2θ region suggest efficient pillaring. The zirconium pillared catalysts in which the pillaring process carried out at room temperature possess large d-spacing than the one pillared at high temperature. Exchange of rare earth metals such as La, Ce and Sm before pillaring improves the acidity and d-spacing values to some extent but lowers the catalytic activity of zirconium pillared clays. Zirconium pillared clays at room temperature are found to be very effective catalysts for the catalytic benzylation of benzene with benzyl chloride. Among the various rare earth exchanged forms, the Sm exchanged Zr pillared montmorillonite shows the highest activity and the least activity is shown by Ce exchanged one. This may be due to the highly basic nature of cerium oxide formed after calcinations.

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