



Characterization of Aluminosilicates (Zeolites) by Laboratory Screening Tests for Selective Synthesis of Value Added Products: Case Studies

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Available online at: www.isca.in

Received 5th June 2013, revised 28th July 2013, accepted 15th August 2013

Abstract

Synthetic zeolites are widely used in chemical industries for the manufacture of value added products because of their acidic and sorption properties. In this work zeolite mordenite metal impregnated mordenites catalyst's samples are investigated for alkylation of benzene to cumene. The effect of varying process parameters and different alkylating agents on conversion and selectivity are presented. The alkylation of aniline with methanol to Monomethyl aniline (NMA) and N, N DMA (dimethyl aniline) is also studied. The Arrhenius activation energy for parent and modified catalysts are compared and discussed considering the extent of modifier species.

Keywords: Synthetic zeolites, sorption, mordenites catalyst's, cumene.

Introduction

Catalysis is one of the most important areas of research in academia and technology. It is the most important technology in environment protection and key to chemical transformations. The catalyst market is divided into four main sectors: environmental catalysts (industrial and automobile environmental catalysts), chemicals, petroleum refining and polymerization. More than 90 % of production processes in industry are catalyzed using homogeneous, heterogenized homogeneous or heterogeneous catalysts. Among these major market share is of heterogeneous catalysts. Improvement in catalyst technology demands focus on lowering energy requirements via higher selectivity, more moderate temperature or pressure, and a reduced number of unit operations in most significant areas of applications.

Catalysts the materials which enhance the rate of a chemical reaction by reduction in the requirement of activation energy play a major role in science of chemistry. The greater portion of chemical feedstocks produced in the world are obtained through catalytic reactions on crude oil, natural gas, and coal. Suitable catalysts are crucial in the commercial-scale production of many plastics, drugs, foodstuffs, and specialty chemicals. The increasingly important field of biosynthesis is based on remarkable specific and efficient enzymatic catalysts. Catalytic reactions are divided into the two main categories of homogeneous and heterogeneous. A heterogeneous catalyst is a suitable chemical compound that is insoluble in the reaction medium. The catalyst may be pure, mixed with the other catalysts, or dispersed on an inert support. Some common heterogeneous catalysts are metals, metal oxides, zeolites, ion-exchange resins, phosphates, clays. There are reports of different types of catalysts' usages for diversified applications in literature including photocatalytic reaction¹⁻¹⁰. The advantages

in using heterogeneous catalysts are their comparatively low cost, ease of recovery, and adaptability to either batch or flow reactors. Zeolites are porous crystalline framework materials containing pores of molecular size (5-12 Å or 0.5 -1.2 nm). They have ability to absorb water and release it upon heating. Conventional zeolites are based on silicate framework in which substitution of some of the Si with Al (or metals) leads to negative charge on the framework, with cations (usually Na or other alkaline or alkaline earth metals) within the pore structure. This leads to another important property, ion exchange, where metal ions in the pore structure can be replaced by other cations (e.g. metal, ammonium, quaternary ammonium).

The zeolites frameworks are networks composed of tetrahedral T atoms (T = Si, Al, etc) linked by oxygen ions. A common building block of zeolites structures consists of 3, 4, 5 and 6 member rings (n-MR). Each n-MR consists of n atoms linked in a ring by O ions and thus actually has 2n atoms; thus a 6-MR has 12 total atoms. The zeolites structures are arranged such that they form larger rings that represent the molecular pores—commonly 8-, 10 – and 12-MR and respectively known as small, intermediate and large pores. Small pore zeolites will generally allow n-paraffins to be adsorbed, while large pore zeolites allow all highly branched paraffins to be adsorbed as well. Intermediate pore zeolites are just that, allowing some branched chain but not highly branched paraffins to be adsorbed. Thus zeolites are part of the larger class of materials called *molecular sieves*, which allow mixtures of molecules of differing structures to be separated. Zeolites occur naturally and are generally formed in alkaline environments from volcanic sediments and materials. These are synthesized in the chemical laboratory by researchers under favorable synthetic conditions and using convenient starting chemical compounds. Faujasite (type Y), mordenite and ZSM-5 type's zeolites find industrial applications on a larger scale.

Industrial chemical processes from the beginning have moved towards a more efficient use of resources and an improvement of selectivity, because both aspects correspond to an improvement in process economics. Catalysis was a fundamental component of this innovation and therefore almost all new developments in catalytic industrial processes fall within the area of interest of environmental catalysis. Eco-efficient processes in clean and unconventional media are one of the main areas of possible industrial innovation for environmental catalysis and sustainable (green) chemistry. Process simplification is a challenge for all industrial syntheses, because it allows lowering of energy use, reduction of waste, and improvement of safety and process economics¹¹.

Phenol is a large volume chemical because of its applications in various polymer syntheses. The conventional and commercial route is a three step process via cumene and cumene hydroperoxide. Cumene (isopropyl benzene), the precursor for phenol is industrially produced by using solid phosphoric acid catalyst. However, there are limitations in the use of this catalyst like: the catalyst cannot be regenerated, the moisture content has to be regulated precisely to avoid leaching and deactivation of the catalyst, transalkylation of diisopropylbenzene (formed to an extent of 5 wt %) with benzene cannot be carried out and environmental problems associated with the disposal of phosphoric acid sludge.

In this paper two cases of zeolite catalyzed reactions namely isopropylation of benzene and N-alkylation of aniline with methanol are investigated using MOR and phosphorous doped MOR at atmospheric pressure.

The crystallographic composition of the unit cell in Na-mordenite is $\text{Na}_8 [\text{Al}_8\text{Si}_{40}\text{O}_{96}] 24 \text{ H}_2\text{O}$. It has orthorhombic symmetry with unit cell parameter $a = 18.1$, $b = 20.5$ and $c = 7.5 \text{ \AA}$. It has void volume = 0.14 cc g^{-1} , aperture size $5.8 \times 7.0 \text{ \AA}$ and framework density of T atoms / $1000 \text{ \AA}^3 = 17.2$ (where T is Si or Al). The crystallographic composition of unit cell of MFI (ZSM-5) zeolite is $\text{Na}_n [\text{Al}_n\text{Si}_{96-n}\text{O}_{192}] \sim 16 \text{ H}_2\text{O}$ with $n < 27$. It has orthorhombic symmetry with unit cell parameters $a = 20.1$, $b = 19.9$ and $c = 13.4 \text{ \AA}$. Having void volume = 0.27 cc g^{-1} , aperture size $5.2 - 5.3$ (zigzag near circular) and $5.3-5.8$ (straight, elliptical) with frame work density of T atoms / $1000 \text{ \AA}^3 = 17.9$ ¹².

Material and Methods

Experimental: Zeolite synthesis (Na-Mordenite): Synthesis of siliceous mordenite was carried out hydrothermally from the system containing $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ at 120°C on crystallization for 96 h¹³. 168.2 g of sodium silicate (27.2 % SiO_2 , 8.4 % Na_2O , and 64.4 % H_2O) was diluted with 200 g of deionised water. An acidic aluminum sulphate solution was made by taking 12.6 g of salt. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in 226 g of deionised water. This solution was then slowly added under stirring to the previously prepared sodium silicate solution. The

reaction mixture was further intensively stirred for 1 h. The resulting gel having $\text{pH} = 11 \pm 0.2$ was then transferred to a stainless steel autoclave. The autoclave was closed and kept in a static air oven at 120°C . After the gel was crystallized for 96 h under static conditions, the crystallization process was terminated by quenching the autoclave to room temperature. The crystalline solid was separated from the liquid by suction filtration. It was then thoroughly washed with hot deionised water till free of sulphate ions and dried in an air oven at 120°C for 8 h. This sample was further calcined in flowing air at 500°C for 12 h in a static air furnace to obtain Na form of zeolite. The catalytically active protonic form (HM) was obtained by repeated ion exchange (till Na, 80 ppm) with a dilute solution of 5% ammonium nitrate (solution /zeolite ratio being 15). The final product was filtered, dried (in air oven at 120°C for 8 h) and calcined at 500°C for 12h in a flow of dry air. The unit cell composition of fully crystalline mordenite sample in its H form, determined by wet chemical /gravimetric methods and atomic absorption spectrometry (Hitachi, model 8000), was $\text{Na}_{0.33} \text{H}_{6.1} [(\text{AlO}_2)_{6.44} (\text{SiO}_2)_{41.56}] 18 \text{ H}_2\text{O}$ (absolute Al = 2.23 mmole /g)

Preparation of phosphorous modified mordenite catalysts (PHM): These samples were prepared by impregnating HM zeolite with appropriate quantity of ortho-phosphoric acid aqueous solution. The well homogenized slurry was slowly evaporated at 98°C for 12 h and calcined in the muffle furnace at 460°C for 10 h to give the corresponding catalyst in the oxide form. All samples were equilibrating with water vapor, before further characterization by placing them over a saturated ammonium chloride solution for 24 h at 25°C .

Characterization: Crystalline phase identification was done by recording XRD patterns on a Philips diffractometer (PW -1730) using $\text{CuK}\alpha$ radiation ($\lambda = 1.54014 \text{ \AA}$). The morphology of the modified catalysts was examined by SEM, scanning electron microscopy (Cambridge stereoscan, Model -150). Samples were mounted on an aluminum peg coated with an Au-Pd evaporated film. Sorption measurements were carried out in an all glass McBain -Baker type gravimetric apparatus using silica spring (sensitivity = 50 cm/g) balance. Prior to sorption measurements, a 50 mg sample pressed into a pellet was activated at 400°C for 4 h under vacuum at 10^{-6} torr. It was cooled to ambient temperature (25°C) under vacuum and was contacted with a sorbate vapor at $P/P_0 = 0.5$ and 0.8 . Equilibrium sorption capacities were noted over a period of 2 h. The thermo gravimetric curves of HM and PHM zeolites were recorded on SETARAM PC92 thermal analyzer in temperature range of 25 to 1000°C in flowing air with heating rate of $10^\circ\text{C} / \text{min}$. For scanning the curves 30 mg sample was used in a platinum crucible. Aluminum was used as a reference material. The total acidity of HM and PHM zeolites was estimated by temperature programmed desorption (TPD) of NH_3 . TPD measurements were done using a stainless steel micro-reactor connected on-line to a gas chromatograph (AIMIL)¹⁴. Figure 1 indicates TPD profiles of H-mordenite and phosphorus doped H-mordenite zeolites.

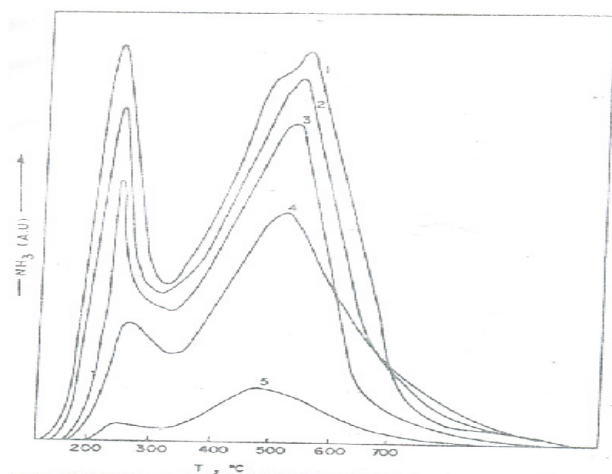


Figure-1

Temperature programmed desorption of ammonia spectra for HM and PHM zeolites

Catalytic activity evaluation (Isopropylation of benzene):

Binder free catalyst powder was pressed (3000 bar pressure) into a tablet, crushed and sieved to 10-22 mesh size and used for catalytic reactions at ambient pressure. 2 g of catalyst was positioned in a down-flow integral fixed bed silica-reactor maintained at constant temperature. The mixture of analytical grade benzene and isopropanol in the desired molar proportion and at a specific WHSV (h^{-1}) (weight hourly space velocity) was passed from the top using a syringe pump (sage instruments USA). The reaction temperature, WHSV and feed composition was optimized prior to this study and these were: reaction temperature = 210°C , WHSV = 2.2 h^{-1} and feed composition benzene to isopropanol molar ratio = 8. Under these optimum conditions the different zeolites (parent catalysts and modified catalyst) were evaluated. The liquid products were collected by circulating ice cold water in the condenser. The liquid products were analyzed isothermally at 125°C using Shimadzu gas chromatograph (Model GC 15 A) fitted with an Apiezone L250 ($1/8'' \text{ ID} \times 2 \text{ m}$) column and FID detector. Gaseous products were analyzed using porapak Q ($1/8'' \text{ ID} \times 6'$) column under programmed temperature. The liquid products identified were aliphatic, unreacted benzene, toluene, C_8 aromatics, cumene (isopropyl benzene i.e., IPB), n-propyl benzene i.e. nPB, $\text{C}_9\text{-C}_{11}$ aromatics and *para* and *meta* diisopropyl benzenes (summarized as Σ DIPB) and traces of higher boiling fractions (triisopropyl benzene).

Effect of alkylating agent: The alkylation of benzene was also carried out with different alkylating agents at mole ratio of benzene to alkylating agent = 7.32 for estimation of their Arrhenius activation energy. The figure 3, 4 and 5 represent the Arrhenius plots for isopropanol n-propanol and propylene as alkylating agents. From the values of the slope of these plots the Arrhenius activation energy is calculated to be $18.5 \text{ K cal g}^{-1}$, $90.71 \text{ K cal g}^{-1}$ and $24.59 \text{ K cal g}^{-1}$ for isopropanol, n-propanol and propylene respectively. When propylene was used as an

alkylating agent conversions are higher even at 190°C and at higher temperature unreacted propylene was observed in product stream. When isopropanol was used, higher temperature was needed for the same conversions. However, the activity of n-propanol was maximum around 275°C . The product pattern in all these cases is similar, irrespective of the alkylating agent; isopropyl benzene is the major component. The product from n-propanol was largely rearranged isopropyl benzene, as expected for carbonium ion process in which a primary cation is rearranged to a secondary cation. Special experiments over H-MOR zeolite were carried out using longer duration of time by passing propylene directly and by passing through H_2O trap while benzene was fed at the desired rate from the top of the reactor at the preheater zone. These runs were carried out at identical experimental conditions (Temperature = 172°C , WHSV = 1.82 h^{-1} , Benzene to propylene molar ratio = 7.32 and at atmospheric pressure) The results of the run are depicted in Figures 6 and 8 show the catalytic performance when propylene is passed through H_2O trap and figures 7 and 9 Show the catalytic performance when propylene is passed directly (not through H_2O trap). Figure 6 and 7 show the propylene conversion to isopropyl benzene (IPB), propylene conversion to diisopropyl benzene (DIPB) and Σ alkylated products /alkylates (summation of IPB, n-PB (n-propyl benzene) and DIPB. The figures 8 and 9 show the ratio of DIPB/IPB and IPB/IPB+ n-PB. It is seen that there is decrease in the formation of isopropylene benzene and increase in the diisopropylbenzene when moist propylene is passed the catalyst bed (passed through H_2O trap). The impurities (toluene, C_8 aromatics and n-PB) are reduced indicating neutralization of some acidic sites with water molecules. The increase in DIPB concentration is due to lower acidity. Both high temperature and acidity are needed for reversible transalkylation reaction. Temperature being constant in reaction with and without water vapour, the higher concentration of DIPB may be related to the lower number of acid sites due to which transalkylation and dealkylation of DIPB is reduced. The presence of water (steam) may also facilitate easier removal of DIPB from the pores. This explains the increased yield of DIPB in presence of water. At longer duration for about 14 hours on stream, conversion to IPB and DIPB decreased for both the cases (propylene passed directly and propylene passed through H_2O trap which is called as moist propylene). Isopropylation of benzene is a multi-step sequential reaction and the main reaction scheme involved may be represented as¹⁵: i. Isopropanol \rightarrow Propene + Water, ii. Benzene + Propene \rightarrow Cumene, iii. Cumene + Propene \rightarrow Diisopropylbenzene, iv. Diisopropylbenzene + Propene \rightarrow Triisopropylbenzene, v. Triisopropylbenzene + Benzene \rightarrow 2 Diisopropylbenzene, vi. Diisopropylbenzene + Benzene \rightarrow 2 Cumene, vii. 2 Cumene \rightarrow Diisopropylbenzene + Benzene.

The reaction is known to proceed through activation of alkene by the catalyst. The activated alkene then reacts with benzene or monoalkylbenzene to form cumene and di-isopropyl benzenes.

Table 1
Equilibrium sorption capacities and void volume of HM and PHM zeolites

sorption [#] capacities and void volume Table 1: Equilibrium of HM and PHM zeolites Zeolite@	Water	n-hexane	Benzene	Cumene	n-PB	n-BA ^{&}	Void Volume cc g ⁻¹
HM	9.33	0.85	1.24	0.38	0.49	1.58	0.1082
PHM(0.32)	8.79	0.75	1.05	0.44	0.52	1.51	0.0962
PHM(0.64)	9.82	0.79	0.93	0.39	0.46	1.27	0.1012

#: Sorption values in m mole g⁻¹, @: Figures in parenthesis indicate % phosphorous impregnated, & : P/P₀ = 0.8

Table-2
Alkylation of benzene with isopropanol: product distribution over HM zeolite

T ° C	150	185	215	230	250	275	300
Aliphatic	0.40	0.48	0.31	0.32	0.11	0.32	0.80
Benzene	90.86	86.50	82.80	83.0	84.40	87.0	91.10
Toluene	-	-	-	0.03	0.06	0.18	0.45
C ₈ -aromatics	-	-	0.02	0.08	0.22	0.54	0.87
Isopropyl benzene(IPB)	5.66	7.40	15.10	15.60	13.75	9.84	4.40
n-propyl benzene(nPB)	0.01	0.02	0.02	0.14	0.65	1.40	2.06
C ₉ -C ₁₁ aromatics	-	-	0.01	0.04	0.1	0.32	-
DIPB	2.96	5.60	1.72	0.80	0.63	0.32	0.34
HBF [@]	-	-	0.06	0.01	0.04	0.13	-
% prop conv to IPB	31.41	41.07	83.80	86.58	76.32	54.61	24.42
% Total prop conv	55.79	87.21	98.04	93.92	85.08	65.01	38.64
% Selectivity to IPB	56.30	47.09	85.47	92.18	89.69	84.0	63.19

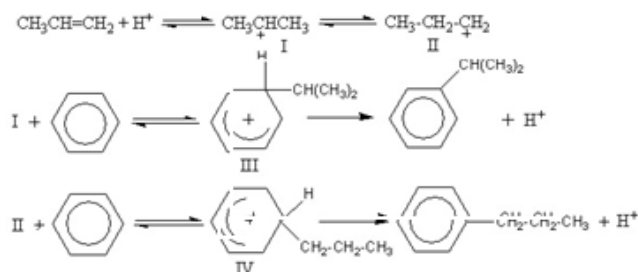


Figure-2

Mechanism of formation of isopropylbenzene (cumene) and n-propylbenzenes

The reaction is known to proceed through activation of alkene by the catalyst. The activated alkene then reacts with benzene or monoalkylbenzene to form cumene and di-isopropyl benzenes. The above reaction scheme (figure 2) depicts the mechanism of formation of isopropyl benzene (cumene) and nPB (n-propyl benzene) at the zeolite surface and it is the Brønsted acid (H⁺ on zeolite surfaces) catalyzed reaction. Secondary carbonium ion, favored by stability considerations results in transient species III which gives isopropyl benzene at the Brønsted acid site¹⁶. The transient species IV results in the formation of n-propyl benzene. The Arrhenius activation energy for the alkylation of benzene with isopropanol, n-propanol and propylene were calculated using expression: $K = F/W \ln 1/1-X$ where K =

reaction rate constant, F is the moles of isopropanol passed per hour, W is the weight of catalyst and X is the fractional conversion. Accordingly the plots of $-\ln K$ versus $1/T$ ($^{\circ}K^{-1}$) are shown in figures 3, 4 and 5. From the slopes of the plots the activation energy was deduced. Figure 3, 4 and 5 show the plots for isopropanol, n-propanol and propylene when used as alkylating agents.

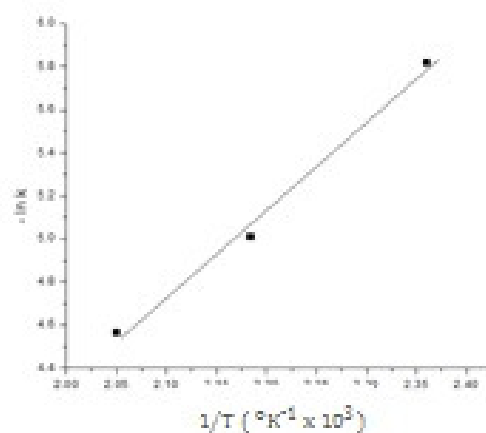


Figure-3

The Arrhenius plot of alkylation of benzene with isopropanol

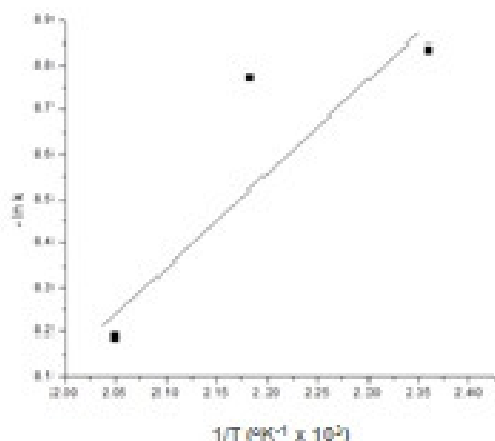


Figure-4

The Arrhenius plot of alkylation of benzene with n-propanol

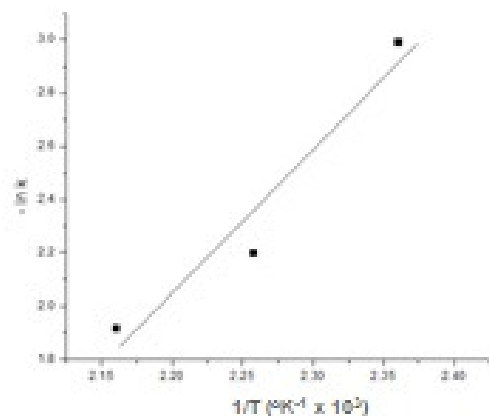


Figure-5

The Arrhenius plot of alkylation of benzene with propylene

Reaction conditions: Temperature = 172 °C, WHSV = 1.82 h⁻¹, Benzene to propylene molar ratio = 7.32 Pressure = 1 atmosphere.

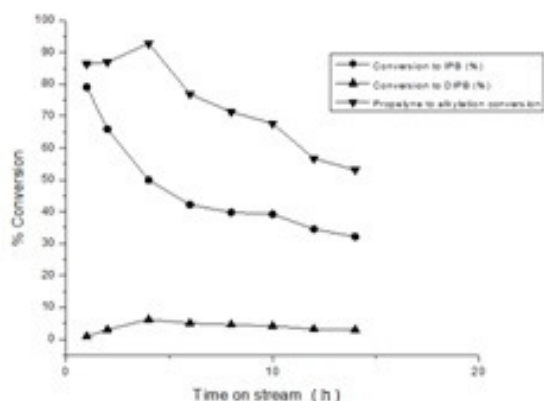


Figure-6

Conversion of propylene (%) versus time-on-stream (h) (Direct passing of propylene)

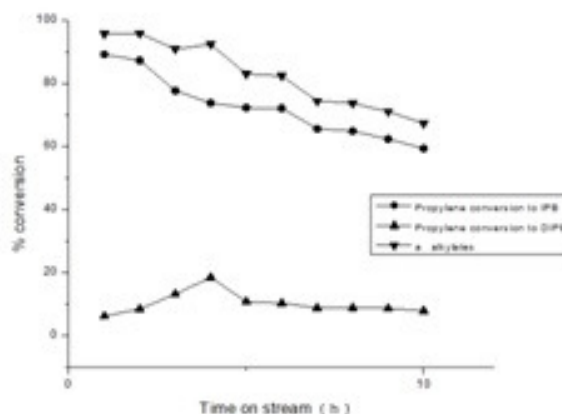


Figure-7

DIPB / IPB (mole) and IPB / IPB+n-PB versus time-on-stream (h) (Direct passing of propylene)

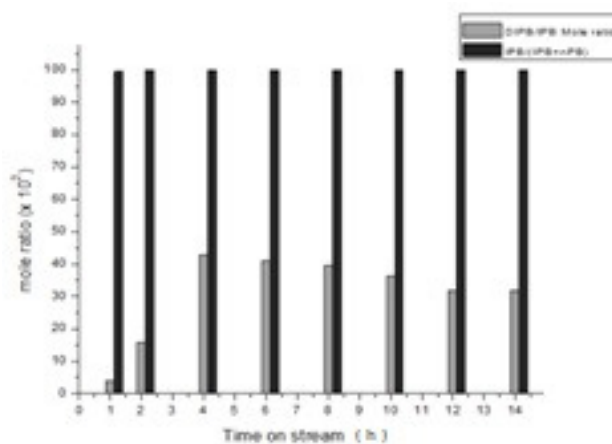


Figure-8

Conversion of propylene (%) versus time-on-stream (h) for moist propylene (Propylene is passed through H₂O trap)

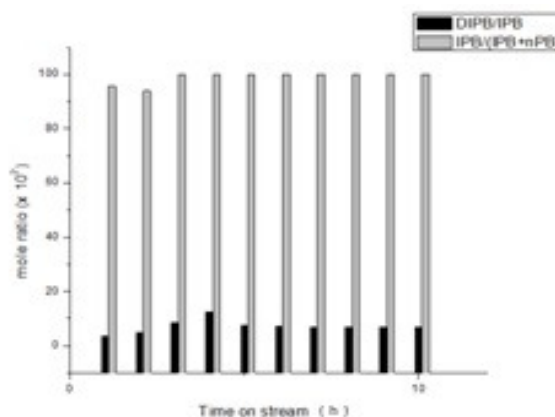


Figure-9

DIPB/IPB (mole) and IPB/IPB+n-PB versus time-on-stream (h) for moist propylene (Propylene is passed through H₂O trap)

Results and Discussion

XRD investigation of as synthesized samples showed a specific diffraction patterns assigned to mordenite structure³. The modification of mordenite by phosphorous doping did not show any shift in the diffraction angle 2θ and there was no loss of crystal structure not depicted here. SEM photograph showed the crystallite size in the range of 1-3 μm . Sorption data for HM and PHM zeolites of organic compounds at $P/P_0 = 0.5$ (for nBA, $P/P_0 = 0.8$) is shown in the table 1. nBA (n-butylamine) gives an estimation of the acid sites present in the solid catalysts like zeolites¹⁷. The sorption capacity of nBA was found to decrease with increasing amount of phosphorous loaded. This could be due to increase in concentration of POH groups of phosphorous species covering the bridged hydroxyl groups (as depicted below in figure F)¹⁸. The acidity of the zeolites was estimated by TPD of NH_3 as well. Isopropylation of benzene is a multi-step sequential reaction and the main reaction can be shown as:

Effect of moist propylene (Propylene passed through H_2O trap): Figure 6 and figure 8 respectively show the propylene conversion to isopropyl benzene (IPB), propylene conversion to diisopropyl benzene (DIPB) and Σ alkylated products /alkylates (summation of IPB, n-PB (n-propyl benzene) and DIPB when propylene was passed directly (not passed through H_2O trap) and for use of moist propylene (propylene was passed through H_2O trap). Figure 7 and figure 9 depict the ratio of DIPB/IPB and IPB/IPB+n-PB for the same experiments for propylene and moist propylene respectively. From figures 7 to figure 9 it is seen that there is decrease in the formation of isopropylene benzene and increase in the diisopropylbenzene when moist propylene is passed through the catalyst bed (passed through H_2O trap). The impurities (toluene, C_8 aromatics and n-PB) are reduced indicating neutralization of some acidic sites with water molecules. The increase in DIPB concentration is due to lower acidity. Both high temperature and acidity are needed for reversible transalkylation reaction. Temperature being constant in reaction with and without water vapour, the higher concentration of DIPB may be related to the lower number of acid sites due to which transalkylation and dealkylation of DIPB is reduced. The presence of water (steam) may also facilitate easier removal of DIPB from the pores. This explains the increased yield of DIPB in presence of water. At longer duration for about 14 hours on stream, conversion to IPB and DIPB decreased for both the cases (propylene passed directly and propylene passed through H_2O trap which is called as moist propylene

The N-alkylation of aniline with methanol: The N-alkylation of aniline with methanol was carried out over H-mordenite and PHM (0.32 % doped phosphorous over H-mordenite) and PHM (0.64 % doped H-mordenite). These catalysts are designated as MI, MII and MIII respectively. The Arrhenius activation energy plots of the reactions over these catalysts are shown in figures 11, 12 and 13 respectively (Reaction conditions: methanol: aniline (molar ratio) = 4; WHSV= 3.15 h^{-1} ; Pressure

= Atmospheric). It is reported that elemental phosphorus binds the zeolite framework through oxygen causing reduction in acidic sites [8] as depicted below figure 10:

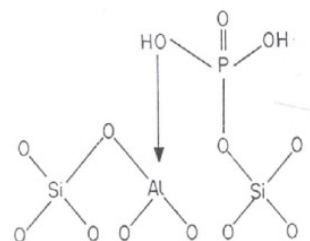


Figure-10

Formation of phosphorous complex with zeolite framework

In the present investigation it was noted from TPD of NH_3 desorption spectra that there is decrease of accessible Al to NH_3 molecule (m mol g^{-1}). It was 1.72 for HMOR, 1.44 for PHM (0.32 P) and 1.08 for PHM (0.64P) where 0.32 and 0.64 stand for % of phosphorous doping over H-mordenite zeolite catalyst. The purpose of the present investigation was to compare the reactivity of H-mordenite and phosphorous doped H-mordenite catalyst. Their Arrhenius activation energy are calculated from figures 11,12 and 13 using expression : $K = F/W \ln 1/1-x$ where K is the reaction rate constant , F is the moles of feed passed per hour, W is the catalyst weight in gram and x is the fractional conversion. Accordingly the plots of $-\ln K$ (mole h^{-1}) versus $1/T$ ($^{\circ}\text{K}^{-1}$) is depicted in above figures. From the slopes of the plots the Arrhenius activation energy is calculated to be: 31.75 K cal g^{-1} for H-mordenite (plot MI) 24.87 K cal g^{-1} for PHM (0.32) and 6.75 K cal g^{-1} for PHM (0.64). This indicates that there is linear reduction in activation energy for N-alkylation of aniline as assessable Al is decreased due to increase in coverage of acid sites (the % acid sites covered due to modifier species is 16.28 for H-mordenite, 37.21 for PHM (0.32) and 50 for PHM (o.64). The reaction mechanism for aniline alkylation is depicted in figure 14.

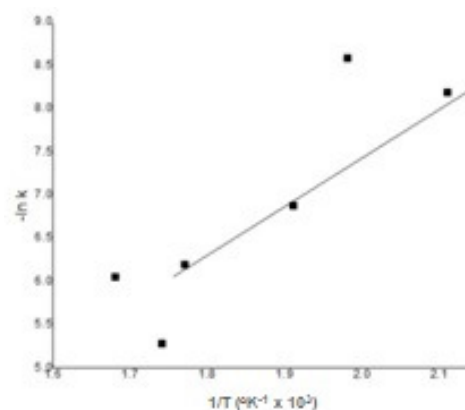


Figure-11

The Arrhenius plot of aniline methylation for MI (H-mordenite zeolite)

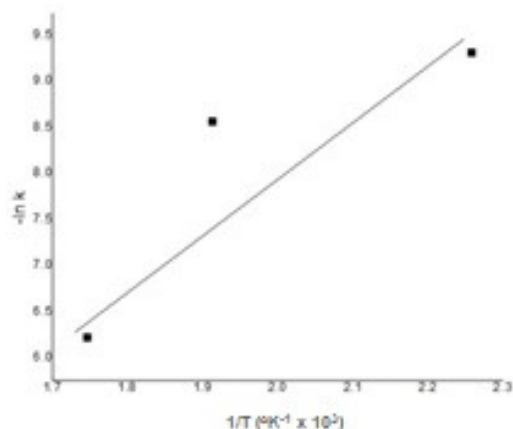


Figure-12

The Arrhenius plot of aniline methylation for MII (H-mordenite doped with 0.32 wt % phosphorous)

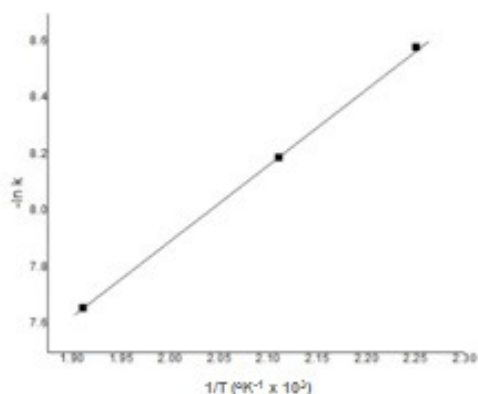


Figure-13

The Arrhenius plot of aniline methylation for MIII (H-mordenite doped with 0.64 wt % phosphorous)

Table-3
Catalytic performance of the HM and PHM zeolites for aniline methylation

Catalyst #	MI	MII	MIII
% Conversion of aniline	30.8	13.22	2.08
% Selectivity to NMA	61.88	74.13	91.34
% Selectivity to NNDMA	26.99	24.96	5.28

NMA: Monomethyl aniline and NNDMA: Dimethyl aniline

Table 3 explains the results (catalytic performance) of the reaction for aniline methylation (Reaction conditions: Temperature = 300 °C methanol: aniline molar ratio =4, WHSV = 3.15 h⁻¹; Pressure = Atmospheric). From above table there is clear indication that the conversion is linearly decreased where as selectivity to monoalkylated product NMA is increased with doping of phosphorous over H-mordenite catalyst. The formation of di alkylated product NNDMA is however decreased drastically for higher doping of phosphorus over H-mordenite catalyst. The selectivity ratio (NMA/NNDMA)

calculated for above three catalysts is in the increasing order of MIII > MII > MI and total N alkylated products (NMA+NNDMA) as: MII > MIII > MI

This implies that a 0.32 wt % phosphorous doping is advisable.

Reaction mechanism of aniline methylation:

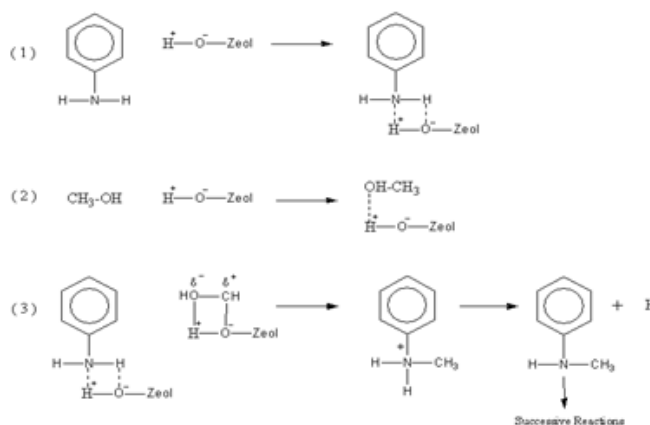


Figure-14

Reaction mechanism for aniline methylation over zeolite catalyst

The reaction mechanism of aniline methylation was proposed considering aniline is in adsorbed state and is in equilibrium with the zeolite surface. The reaction involves adsorbed molecule. If the nitrogen of the aniline interacts at the electron withdrawing site (e.g. proton) enough Pi -electron shift or actual electron transfer could occur to generate species with a significant degree of the + ve charge. Attack of such species on a +vely charged carbocation would not be expected because of columbic repulsive forces. However, adsorption of aniline in the field of sorption potential of surrounding lattice within the molecular sieve pores (in zeolites pores) can occur¹⁹. Thus aniline competes for methanol adsorption on the intracrystalline surface within micro pores. At high temperature (> 200 °C) significant desorption of aniline occurred and the remaining aniline is adsorbed undissociatively. Thus enough active sites of the catalyst is available so that methanol could compete for the adsorption and generate an electrophile (CH₃ δ +ve). The electrophilic attack of the nitrogen atom of aniline gives N-methyl aniline.

Conclusion

Acidity and pore volume of phosphorous modified HM zeolite decreased. The reduction in activity of phosphorous doped zeolite is correlated to the elimination of surface hydroxyl groups due incorporation of impregnated material. Among the alcohols, isopropanol when used as an alkylating agent, showed lower Arrhenius activation energy than n-propanol for isopropylation of benzene to cumene. Reduction in surface

hydroxyl groups eliminates formation of unwanted products in alkylation reaction of aniline with methanol. The use of moist propylene (presence of water) facilitates easier removal of Diisopropyl benzene from zeolite pores. The 0.32 wt % phosphorous doping on H-mordenite showed better catalytic performance for alkylation of aniline with methanol.

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