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Re-usability of zeolites and modified clays for alkylation of cyclohexanol a contrast study

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Abstract:

Organic sulfonic acid treatment of montmorillonite results in micro-pores on the surface of modified clays providing access to acid sites in the interlayer. Performance of modified clay catalysts for alkylation of *para*-cresol with cyclohexanol were compared with microporous zeolites. Phenoldisulfonic acid treated clay catalyst showed maximum activity comparable with that of beta-zeolite. Modified clay- and zeolite-catalysts on reuse for the alkylation exhibited different behaviour. Modified clays showed same activity as in the first cycle while zeolites showed significantly reduced catalytic activities on reuse. Differences in behaviour were further investigated by characterizing the reused samples with TGA, acidity and surface measurements. Used zeolite samples showed considerable variations in acidity, surface characteristics and TGA pattern, which was attributed to the formation of coke. Absence of coke in clays and deposition of coke in zeolites is attributed to difference in their pore architecture.

Keywords:

Zeolite, Modified clay, Alkylation, Organic sulfonic acids, Reusability

1. Introduction:

Zeolites are widely used as solid acid catalysts in the field of heterogeneous catalysis. They have aluminosilicate frame work structure with three dimensional channels possessing acid sites having potential applications in industrial organic transformations [1-4].

Clays are aluminosilicates having two dimensional layered structures with stacked frame work arrangement. In clays, such as montmorillonite, negative charge on the layer arises because of isomorphous replacement of structural Al with divalent Mg and Fe ions. Cations such as Na, Ca and Mg occupy the clay interlayer and neutralize the negative charge [1, 3, 5, 6].

Montmorillonite upon acid treatment undergoes dealumination and forms H^+/Al-exchanged clay, an acid catalyst. There are reports in the literature that treatment of montmorillonite with organic acids generates

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pores on the surface caused by voids due to controlled dealumination in the octahedral layer. The generated pores give enhanced accessibility to the interlayer acid sites [7-15].

Organic acids remove structural Al, essentially through the formation of soluble complexes, a part of which are carried to the interlamellar region on washing with water. In the interlamellar region, they get hydrolysed to Al^{3+} ions which replace the Na ions in the interlayer resulting in Al-clay[13]. Organic acid treatment thus results in a clay retaining most of its cation exchange capacity (CEC). In comparison, mineral acids remove, in addition to Al, the structural Fe and Mg ions. This results in reduced cation exchange capacity and lower acidity. Organic acids thus have an advantage of providing a clay retaining most of its CEC and acidity.[8-14]

Both zeolites and modified clays have been used as catalysts in several organic reactions like acylation, Fries rearrangement, esterification, cracking and methoxylation [16-26].

Alkylation of phenol is one of the most important aromatic reactions both in organic synthesis and chemical manufacturing. The alkyl phenols are widely used as precursors for detergents, pesticides, and additives for fuels, herbicides, polymers, phenolic resins, antioxidants, lubricants, fragrances, thermoplastic elastomers and paints [20, 27-29].

Recently researchers have been exploring the possibility of using environmentally benign catalysts for alkylation [3–5, 30]. In this context, alkylation of *p*-cresol has been studied using environmentally friendly catalysts such as zeolites and clays, wherein the main acidity of the zeolites occur within their pores and in the interlayer region for the clay minerals. The present study aims at comparing the performance and reusability of organic acid modified clay with zeolite for alkylation of *p*-cresol (PC) with cyclohexanol (CH).

2. Experimental:

2.1 Materials method:

Montmorillonite clay sample used in the present study belonged to the Bhuj area, Gujarat, India and is obtained from Ashapura Chemicals. The 2µm fraction of the clay sample [31] was further homogenised with NaCl to get the Na-Clay. Its composition was analysed by ICP-OES after microwave digestion in hydrofluoric acid. It was found to be 42.86% SiO_2, 18.64% Al_2O_3, 9.05% Fe_2O_3, 2.58% MgO and 4.12% Na_2O. [32-34]

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Methanesulfonic acid (MSA), p-toluenesulfonic acid (p-TSA) were obtained from SD fine chemicals and phenoldisulfonic acid (PDSA) from Loba chemicals, India. ZSM-5, Beta-zeolite (HBEA) and Y-zeolite (Y-Z) were obtained from Reliance industries, Vadodara, Gujarat.

2.2 Catalyst preparation:

Clay samples were modified by treating with organic acids MSA, p-TSA and PDSA by following the procedure reported in the literature.[13, 29, 32] 10 g montmorillonite clay was dispersed in 1M 100 ml organic acid and the mixture was subjected to microwave irradiation for 30 min. A maximum power of 800 W was applied to reach 110 ^{0}C in the initial one minute and the same temperature was maintained by applying the required power ranging from 200 to 800 W for 29 min. Then the mixture was cooled to ambient temperature and washed repeatedly with deionized water by centrifugation until the centrifugate becomes neutral. The clay residue was dried at 120 ^{0}C and finely ground. The different organic acid treated modified clay samples were designated as MSA-clay, p-TSA-clay and PDSA-clay.

2.3 Characterization:

The modified clay and zeolite samples were characterized using various physicochemical techniques such as, pyridine FT-IR, TPD-NH_3, TGA, powder XRD, BET surface area, ^{27}Al-MAS NMR and TEM. The samples after the alkylation reaction were recovered and designated as p-TSAR, MSAR, PDSAR for clays and BEAR, ZSM-5R for zeolites respectively. The recovered samples were also characterized by the techniques mentioned which are described below.

Acidities of samples were determined by recording pyridine adsorbed FT-IR spectra. All the samples were activated by degassing at 110 ^{0}C for 2 hours, then cooled under vacuum and saturated with liquid pyridine for 30 min. Samples were again heated to 115 ^{0}C to remove physisorbed pyridine and the spectra were recorded by KBr pellet technique using Shimadzu, IR-Affinity-1 instrument with resolution of 4 cm^{-1} and 40 scans in the wavenumber range of 1600-1400 cm^{-1}. Brønsted and Lewis acidities were evaluated from the peak areas and expressed as mmol/g as given in the literature [32].

The total acidity of modified clays was also evaluated using TPD-NH_3 method. In a typical experiment, 0.1 g of sample was taken in a U-shaped quartz sample tube. The catalyst was heated to 150^{0}C in He(30 cm^3/min) for 2 h. A mixture of NH_3 (90%) and He (10%) was passed at the rate of 30 cm^3/min for 30 min over the catalyst maintained at 60^{0}C. After this the catalyst sample was flushed with He(30 cm^3/min) for 60 minutes. TPD measurements were carried out in the range 100–650^{0}C with heating rate of 10^{0}C/min. Ammonia concentration in the effluent was monitored with thermal conductivity detector [30, 32].

Surface area and pore characteristics of parent clay, zeolites and modified clays were characterized under liquid nitrogen temperature by Quanta Chrome Nova-1000 surface analyser instrument. Adsorption-desorption isotherm measurements were carried out for the evolution of porosity and textural properties. BET, BJH (Barrett–Joyner–Halenda) methods were used to evaluate surface area, pore diameter and pore volume and de Boer t-method (Temkin) for the newly generated micro-pore volume [32].

Structural integrity of the catalyst samples was checked by powder XRD. The data were recorded by step scanning at $2\theta = 0.020^0$ per second from 3^0 to 80^0 on Shimadzu Maxima XRD-7000 X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å).

Thermogravimetric analysis were performed using a Mettler Toledo 851e stare 7.01 TGA-DTA system by applying ramping rate of 5 ^{0}C min^{-1} to the temperature 100 to 650 ^{0}C under flowing air.

A morphological change of montmorillonite before and after treatment with PDSA was recorded using Tecnai-G2 Transmission Electron Microscope (TEM) under 120KV under vacuum mode.

^{27}Al-MASNMR pattern was recorded with resolution of 25Hz and 512 numbers of scans using single pulse JEOL ECX-2 400 MHz magic angle spin nuclear magnetic resonance spectrometer having frequency 104.261 MHz with a 4 mm rotor of spinning speed 10k. The $Al(NO_3)_3$ is used as an external standard.

2.4 Catalytic activity:

The Catalytic activity of all the catalyst samples was studied in microwave reactor, microwave lab station "START-S" from Milestone, Italy, having software which enables the online control of reaction mixture temperature with the aid of an infrared sensor that monitors the temperature by regulation of microwave power output. The maximum variable power up to 1200 W was applied by the microprocessor controlled single-magnetron system.

Initially, the reaction was conducted varying the catalyst amount and mole ratio at different reaction temperatures in the microwave reactor. Under the optimized conditions, ten mmol of PC and ten mmol of CH were mixed with 0.5 g of the catalyst in a microwave reactor vessel with a magnetic stirring bar. The vessel was kept in a microwave reactor and an initial power of 1200 W was applied for 1 minute to achieve reaction mixture temperature of 120 °C. Same temperature was maintained for 29 minutes. After cooling the reaction mixture, 10 mL of toluene was added and stirred for 10 min. Then the mixture of reactants and products were extracted by filtration and analysed using Chemito GC-1000 gas chromatograph having FID with a TR-WAX capillary column of 30 m length, 0.32 mm thickness and 0.55 µm internal diameter [33].

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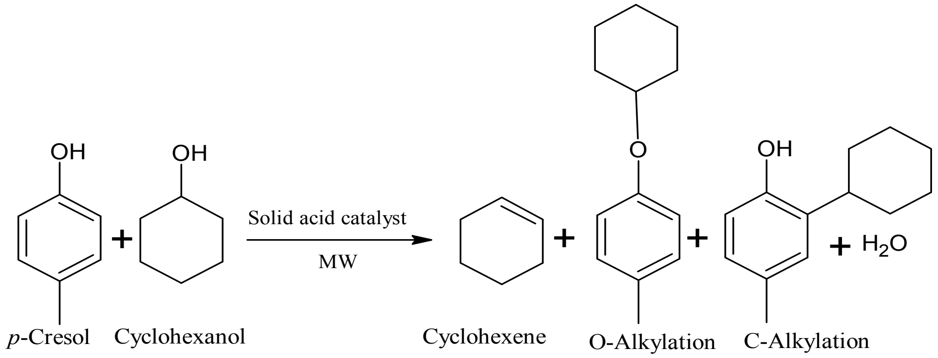
Reaction products formed were confirmed by GC-MS method using, Shimadzu GCMS-QP2010S with a Column: Rtx-5 (30m length, 0.25mm thickness 0.25 µm internal diameter). The chemical reaction with the products formed is shown in scheme-1.

Catalytic activity measurement of samples was performed three times on each sample and mean values were used for calculating the standard deviation. Under the experimental conditions, intra-particle and inter-phase heat and mass transfer were calculated using Mears, Koros-Nowak and Weisz- Prater criteria were found to be negligible [34, 35].

After the completion of reaction, some of the catalyst samples exhibited discoloration. All the used catalyst samples were separated by filtration and once again characterized by the techniques already described. This was to identify the changes that are brought about on the catalyst samples by the reaction. The spent catalyst samples recovered, (p-TSAR, MSAR, PDSAR for clays and BEAR, ZSM-5R for zeolites respectively) were reused to test the repeatability.



Scheme 1: Alkylation reaction carried using solid acid catalysts samples.

3. Results and discussion:

3.1 Acid treated clays catalytic activity:

Alkylation reaction was conducted under optimized conditions after preliminary experiments at different temperatures (in the range of 60 to 180^{0}C), with increase in reaction time (from 5 to 240 minutes) and varying the catalyst amount (0.1 to 1 g). Mole ratio 1:2 of CH to PC was maintained. Typical results are shown for PDSA catalyst in Fig. 1. The trends were almost same for other catalyst samples.

Fig1 (a) shows an initial steep rise in conversion of CH along with formation of cyclohexene. Apparently, initially formed cyclohexene favours the formation of O-alkylated product, O-CH. With increase in time, cyclohexene is used up for C-alkylation. A decrease in the O-CH is also noticed. This continues to form the alkylated products till an equilibrium ratio is reached.

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Fig. 1(b) shows the progress of reaction as a function of temperature. Beyond 160 ^{0}C, almost complete conversion of CH is observed. At 100 ^{0}C, cyclohexene concentration reached a maximum value but the alkylated products formed were in small amounts. Beyond 100 ^{0}C, the cyclohexene formed was consumed for the alkylation favouring C-alkylated product. A simultaneous decrease in the O-CH product is observed beyond 100 ^{0}C.

Formation of different products with the increase in catalyst amount is shown in Fig 1 (c). Almost complete conversion of CH was noticed beyond 0.9 g of catalyst. Formation of cyclohexene initially increased and reached a maximum with the catalyst amount up to 0.4 g, beyond which it was used up preferentially for the formation of C-alkylated product. At this point, a slight decrease in O-CH product is also seen.

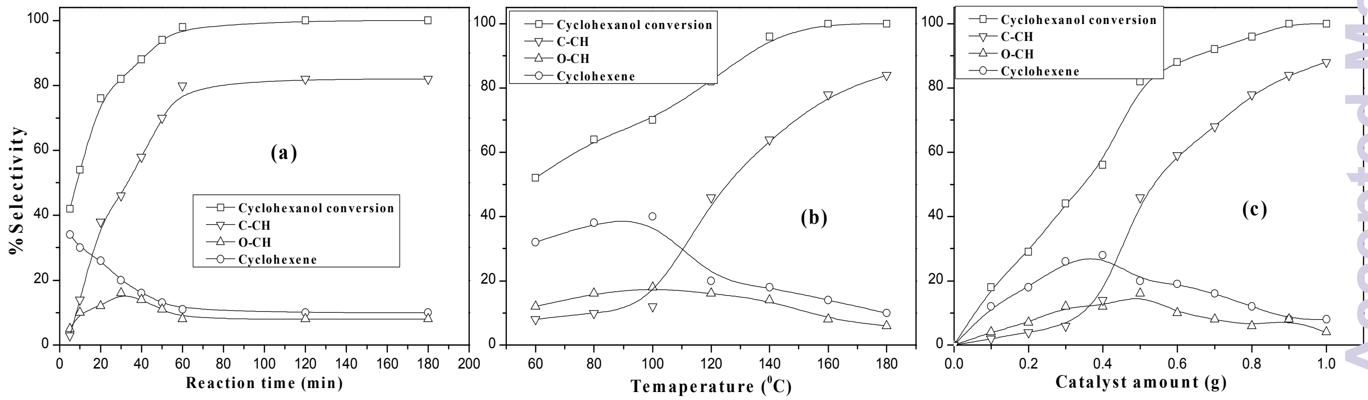

Fig 1: Effect of reaction conditions on alkylation activity of PDSA clay catalyst
(a): Reaction conditions; catalyst 0.5 g; temperature, 120 ^{0}C, mole ratio, PC: CH, 2:1.
(b): Reaction conditions; catalyst 0.5 g; Reaction time, 30 min, mole ratio, PC: CH, 2:1.
(c): Reaction conditions: temperature, 120 ^{0}C, reaction time; 30 min, mole ratio, PC: CH, 2:1.

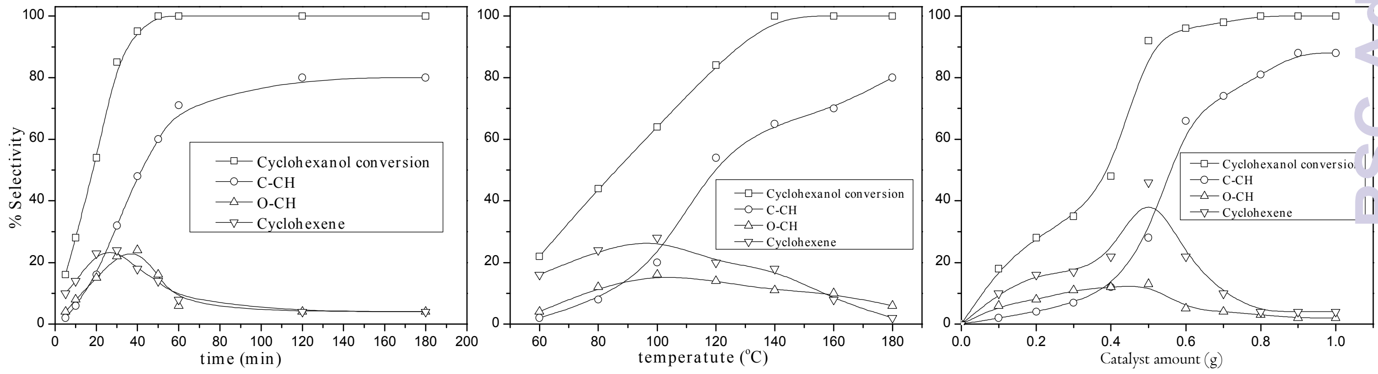

Fig 2: Effect of reaction conditions on alkylation activity of HBEA catalyst
(a): Reaction conditions; catalyst 0.5 g; temperature, 120 ^{0}C, mole ratio, PC: CH, 2:1.
(b): Reaction conditions; catalyst 0.5 g; Reaction time, 30 min, mole ratio, PC: CH, 2:1.

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(c): Reaction conditions: temperature, 120 ^{0}C, reaction time; 30 min, mole ratio, PC: CH, 2:1.

Optimization studies for zeolite samples were also studied. They are presented in Fig.2 the trends were similar to those observed in the case of modified clays.

The results of alkylation carried out at optimum conditions using different catalysts are given in Table 1. Untreated clay did not show any catalytic activity and is not included in the Table. The results in Table 1 show that, modified clays and H-BEA showed almost 100 % conversions of CH, while ZSM-5 and Y-Z showed low conversions.

Table 1 Catalytic activity of different catalyst for alkylation of PC with CH

Catalyst samples	**p-TSA-clay**	**MSA-clay**	**PDSA-clay**	**H-BEA**	**ZSM-5**	**Y-Z**
CH Conversion (%)	96	100	100	100	41	39
O-alkylation	29	26	18	12	9	6
C-alkylation	35	46	61	54	4	12
Cyclohexene (%)	32	28	21	10	18	15

Reaction conditions- mole ratio 1:2 of CH to PC; time 60 min; catalyst 0.5 g; temperature, 120 ^{0}C,

Alkylation is an acid catalysed reaction. In order to explain the improved catalytic activity of clay samples upon modification for alkylation, further studies were made on the modified clays with regard to changes in Brønsted and Lewis acidity and surface characteristics. There are reports in the literature that organic acid treated clays develop pores on their surface and show pore characteristics similar to zeolites but retaining their layer structure [30, 32,34].

Development of pores on the clay surface is explained on the observation of dissolution and chelation of structural Al (III) on treatment with organic acids. The amount of Al leached out upon acid treatment was quantitatively estimated by ICPOES. The structural Al leached out was found to be in the order PDSA (1.14meq/g) >MSA (1.02 meq/g) >p-TSA (0.97 meq/g). A qualitative examination of ^{27}Al NMR spectrum of the untreated montmorillonite sample (Fig. 4) showed the presence of octahedral Al. The removal of Al ions causes voids on surface resulting in the increase in surface area and pore size[10, 11, 13, 23, 30]. The morphology also changes after the treatment as shown by the TEM images (Fig.3).

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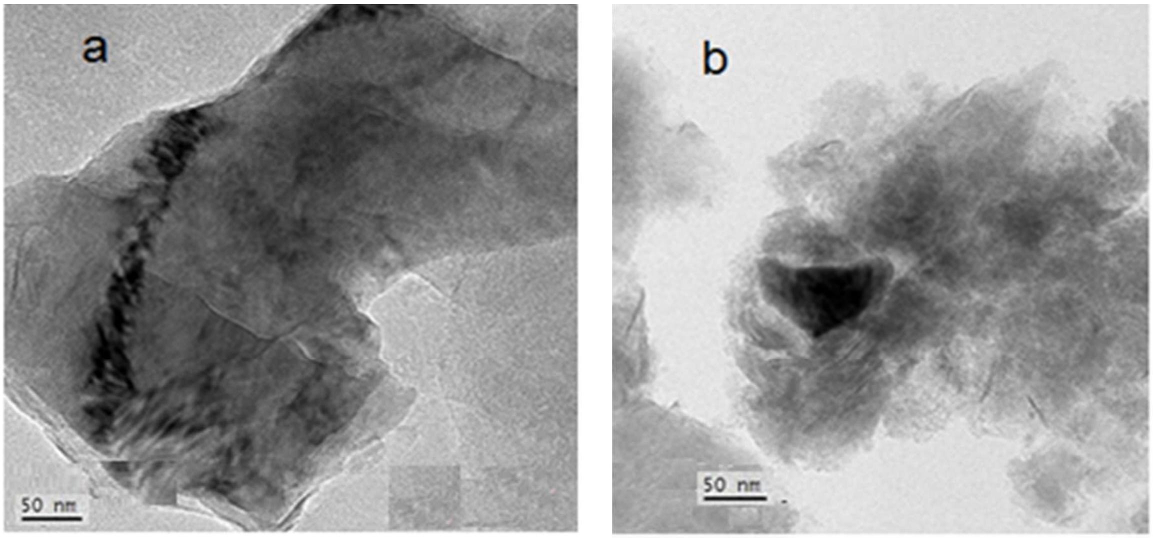

Fig.3 TEM images of (a) Untreated clay, (b) PDSA-clay

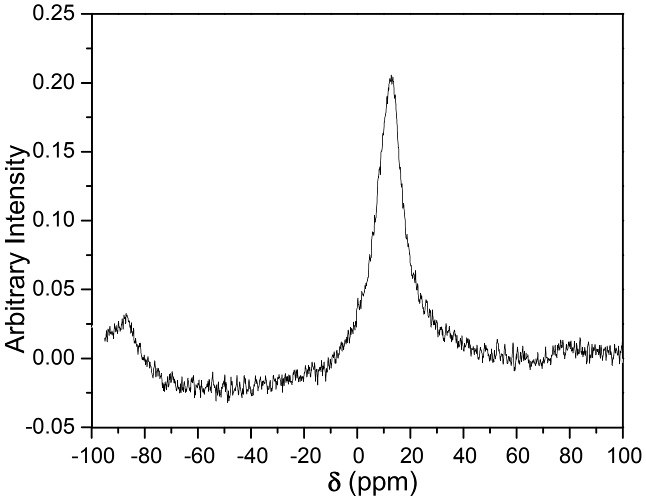

Fig 4 ^{27}Al MAS NMR of untreated montmorillonite clay

Table 2 shows surface area and porosity measurements as determined by BET method and Lewis and Brønsted acidities by pyridine adsorption using FTIR for zeolite samples and the modified clays (spectra provided as supplementary material). Activity of catalyst samples were expressed as average TOF which gives the number of reactant molecules reacted per minute on a single active site of the catalyst.

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Table 2 Surface and acidity characteristics of modified clay samples and zeolites

Clay samples	**S_{BET}** (m^2/g)	**APD** (A^o)	**V_{tot}** (cm^3/g)	**V_{mt}** (cm^3/g)	**B** (μmol/g)	**L** (μmol/g)	**B+L** (μmol/g)	**Total alkylated product** (%)	**Average TOF** (min^{-1})
Untreated	28	50.3	0.078	0.011	-	-	-	-	-
p-TSA-clay	135	35.3	0.120	0.026	70	68	138	64	0.773
MSA-clay	206	32.7	0.195	0.053	69	70	139	72	0.863
PDSA-clay	276	24.0	0.343	0.201	72	68	140	79	0.940
ZSM-5	346	-	0.214	0.076	574	320	894	13	0.024
Y-Z	638	-	0.395	0.300	222	184	406	18	0.074
H-BEA	542	-	0.486	0.132	423	263	686	66	0.160

S_{BET}: BET Surface area (sd;±2.99), APD: average pore diameter (sd;±0.241), V_{tot}: total pore volume (sd;±0.002), V_{mt}: micro-pore volume by de Boer t-method (sd;±0.005), B-Brønsted (sd;±4.11) and L-Lewis acidity (sd;±3.51) as Pyridine FT-IR. B+L acidity (sd;±3.51) and total alkylated product (sd;±0.766)
*sd- standard deviation

Untreated clay sample (Na-clay) did not show any activity because of the absence of acid sites. Modified clays demonstrated better activity for alkylation than the zeolites (Table 2). ZSM-5 and Y-Z showed relatively low activities as shown by the total alkylated product (O-CH + C-CH) formed, while H-BEA showed maximum activity (66 %), among zeolites, almost comparable to that of p-TSA modified clay. The reason for low activity of ZSM-5, though it had higher acidity, is because of the relatively narrow pores compared to HBEA. The low activity of Y-Z is attributed to its low acidity and cage structure.

All the three zeolites had higher acidity values compared to modified clay samples. In the case of zeolites, acid sites are mostly present in the channels in contrast with modified clays where they are present in the interlayer. Since untreated clay does not possess any acid sites, the pores which are generated in the modified clays are able to provide enhanced access to the acid sites present in the interlayer. The enhanced access to the sites is apparently responsible for increased catalytic activities [29-32].

Correlation calculations were made between the total alkylated products formed and the catalyst parameters such as surface area, micro-pore volume, total pore volume, average pore diameter and acidity with the yield of C-alkylated product. Every data represent an average of three replicate samples. The correlation calculations were carried out by standard statistical methods for small sets of data. Correlation coefficients as expressed in r^2 value are shown in Table 3. No correlations were noticed when yield of the alkylated product for all the samples were considered. When clays were considered separately from zeolites, better correlation was observed. Surface area, acidity and total pore volume, micro-pore volume showed high correlation for the modified clays while for zeolites all these parameters poorly correlated with catalytic activity.

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Table 3 Correlation coefficients

Parameters	r^2 for MODIFIED CLAYS			r^2 for ZEOLITES		
S_{BET} (m^2/g)		0.999			0.076	
V_{tot} (cm^3/g)		0.950			0.656	
V_{mt} (cm^3/g)		0.835			0.037	
APD (A^o)		0.942			-	
B (µmol/g)		0.391			0.000	
L (µmol/g)		0.001			0.000	
B+L (µmol/g)		0.998			0.000	
TPD-NH_3						
*Product %	MSA-clay	p-TSA-clay	PDSA-clay	ZSM-5	H-BEA	Y-Z
	(72)	(64)	(79)	(13)	(66)	(18)

*Total alkylated product (O-CH + C-CH)

3.2 Reuse of the used catalysts:

In order to understand the difference in behaviour between two categories of materials with regard to their reusability, the used catalyst samples, recovered from reaction mixture and dried at 80 ^{0}C, were reused in reaction with fresh reagents. The results of alkylation are shown in Table 4 for three more recycles.

Table 4 comparison of catalytic activity of used catalyst samples

Catalyst	Recycle	CH conversion (%)	Total alkylation	Cyclohexene (%)
p-TSA-clay	1st	92	62	30
	2nd	90	62	28
	3rd	91	60	31
MSA-clay	1st	98	72	26
	2nd	98	70	28
	3rd	96	71	27
PDSA-clay	1st	100	79	21
	2nd	100	78	22
	3rd	100	78	22
H-BEA	1st	68	50	10
	2nd	52	36	8
	3rd	43	28	7
ZSM-5	1st	31	12	14
	2nd	26	8	10
	3rd	22	6	10
H-Y	1st	34	20	11
	2nd	30	15	8
	3rd	24	12	4

Reaction conditions; mole ratio 1:2 of CH to PC; time 60 min; catalyst 0.5 g; temperature, 120 ^{0}C

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Zeolites showed considerable reduction in catalytic activity as noticed by the amount of alkylated product formed. This is perhaps due to the formation of coke in case of zeolites. To confirm this, used samples in the 1st recycle were subjected to TGA, acidity and surface measurements. Table 5 shows the results for changes in acidity and surface measurements. The changes noticed are given in parenthesis. Fig 5A and 5B shows variations in pyridine-FTIR acidity and Fig 6A and 6B for changes in TGA plots. Coke formation in case of zeolites is evident by the TGA patterns (Fig 6B). TGA analysis was carried out to find out deposition of any carbonaceous compounds on the catalyst surface during the reaction. It was noticed that there was no significant weight loss for the clay sample. On the other hand, zeolite sample showed 20-30% weight loss after the reaction indicating formation of coke on the surface. Reduction in acidity and surface area (Table 5) provide supporting evidence. Deposition of coke in the zeolite channels may be cause for these reductions in the alkylation (Table 4). On the other hand, modified clays showed no such changes observed in case of zeolites.

3.3 Channels as opposed to open pores in recycling:

Zeolites used in this study are microporous materials and are known to possess cages interconnected through channels for Y- Z and intersecting channels for ZSM-5 and HBEA. Modified clays, however, are known to possess micro- and meso- pores generated by dealumination on acid treatment. The pores formed, in case of modified clays, are open pores on the surface [30, 32, 34]. The different behaviour of two materials for their reusability in the alkylation reaction is apparently due to the difference in their pore architecture. This is further explained below.

The mechanism of alkylation involves the initial formation of cyclohexene from the dehydration of CH (Scheme 2). A part of cyclohexene formed is used up for the alkylation, another part may undergo oligomerization leading to formation of coke and remaining cyclohexene will be present in the reaction mixture. Out of these three, formation of coke is favoured in the channels of zeolites where most of the active sites are located. Furthermore, for several cyclohexene molecules to find the acid sites and get oligomerized to form coke is more probable inside the channels. This clearly explains the coke formation in case of zeolites and also limitation in their reuse for alkylation.

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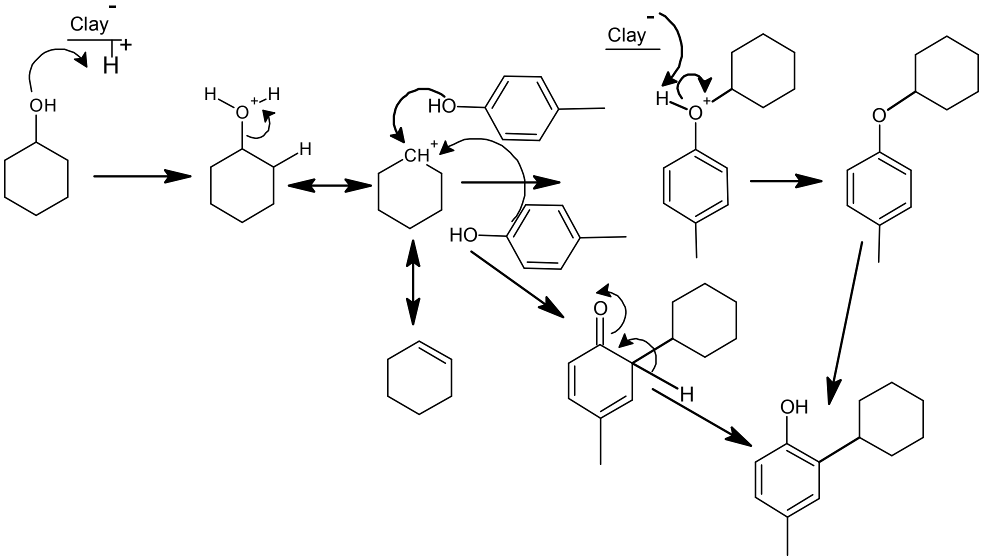

Scheme 2 Possible reaction mechanism for alkylation of PC with CH

In contrast with zeolites, the active sites on the modified clays, are located in the interlayer accessed through the generated pores which are open on the surface. A part of cyclohexene formed on active sites of the clay brings about the alkylation and the rest diffuse into the medium. The diffusing cyclohexene molecules do not find active sites to undergo oligomerization for coke formation. Retardation of coke formation in the case of modified clays and their unchanged catalytic activity for reuse can thus be attributed to their open pores.

Table 5 Surface and acidity characteristics of reused clay samples and zeolites.

Clay samples	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mt} (cm^3/g)	**B** (µmol/g)	**L** (µmol/g)	B+L (µmol/g)
p-TSA-clay	133(2)	0.118(0.002)	0.024(0.002)	69(1)	66(2)	135(3)
MSA-clay	202(4)	0.189(0.006)	0.049(0.004)	67(2)	68((2)	135(4)
PDSA-clay	275(1)	0.332(0.011)	0.198(0.003)	70(2)	67(1)	137(3)
ZSM-5	264(82)	0.153(0.061)	0.049(0.027)	268(306)	202(118)	470(424)
Y-Z	564(74)	0.305(0.090)	0.234(0.066)	168(54)	108(76)	276(130)
H-BEA	384(158)	0.368(0.118)	0.099(0.033)	203(220)	143(120)	346(340)

S_{BET}: BET Surface area, D_p: Average pore diameter, V_{tot}: total pore volume, V_{mt}: micro-pore volume by de Boer t-method, B-Brønsted and L-Lewis acidity as Pyridine FT-IR. The value in ( ) indicates characteristics (before –after reaction)

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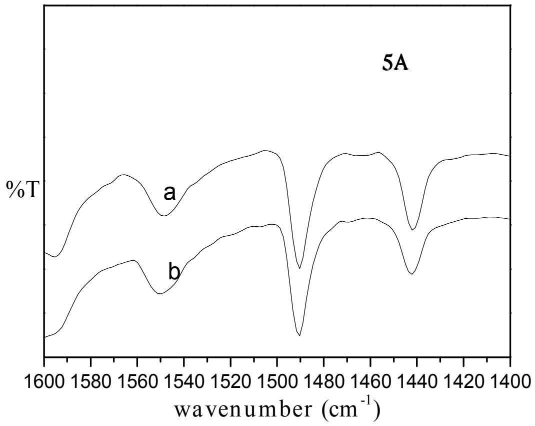

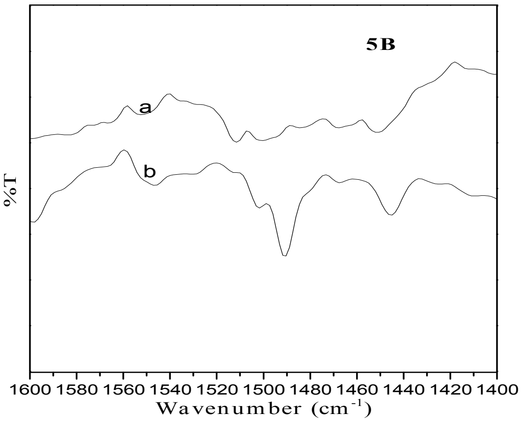

Fig 5A pyridine FT-IR spectra of PDSA clay (a) before and (b) after the reaction
Fig 5B pyridine FT-IR spectra of HBEA (a) after and (b) before the reaction

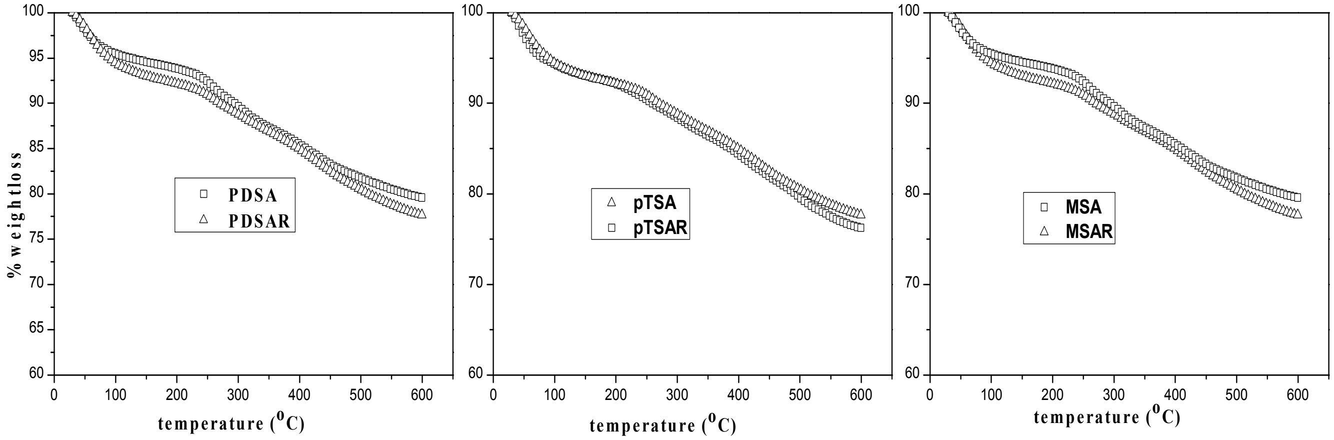

Fig 6A TGA pattern of PDSA, MSA and p-TSA clay samples before and PDSAR, MSAR and p-TSAR samples after reaction

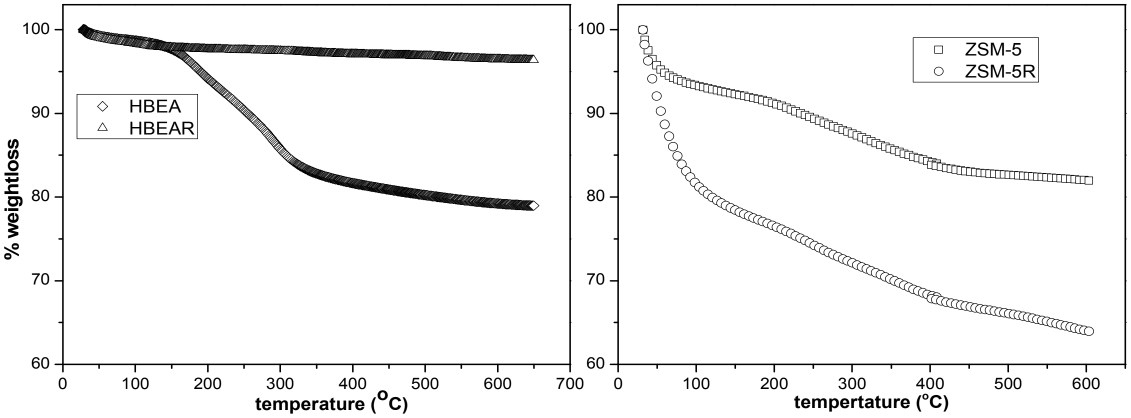

Fig 6B. TGA pattern of ZSM-5 and HBEA zeolites before and ZSM-5R and HBEAR zeolites after reaction

4. Conclusions:

Clays modified with organic sulfonic acids such as PDSA and MSA were found to be more effective than zeolites for alkylation of PC with CH. Reuse of used catalyst samples showed different behaviour for zeolites and modified clays. Zeolites exhibited reduced activity on reuse which was attributed to the formation of coke on the active sites in zeolite channels. Coke formation in the channels is more probable due to the availability of acid sites favouring cyclohexene molecules to oligomerize. Modified clays did not show any change in activity on reuse. Retardation of coke formation in the case of modified clays and their unchanged catalytic activity for reuse is attributed to their open pores.

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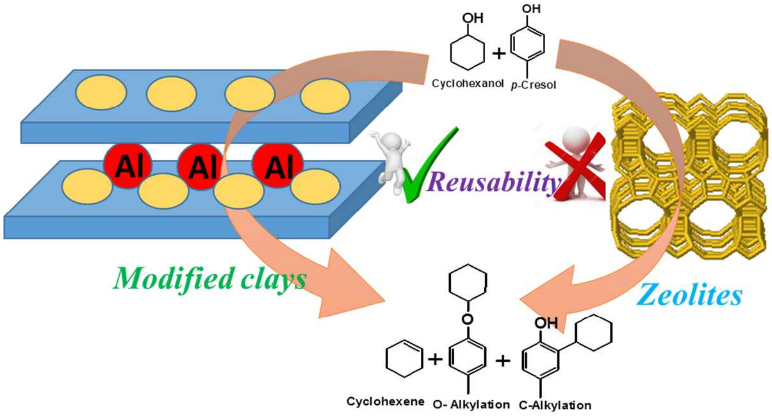
Graphical abstract:



Highlights

- ✓ Organic sulfonic acid treatment generates open pores on surface of clays and these provide access to active sites in the interlayer
- ✓ Modified clays retards formation coke in p-cresol alkylation, while zeolites exhibit diminished activity due to coke formation caused by pore architecture.