Acidity and catalytic activity of rare earth modified Al/Zr pillared clays

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The pillared montmorillonite has been prepared by exchanging Na+ in the interlayer of montmorillonite with Al hydroxy cation followed by calcination. Pillared clays are also prepared after exchanging Na+ ions with Ce, La, Sm-ions and then pillared with aluminium oxides. The surface characterisation of the prepared catalysts has been done using XRD and surface area measurements. To probe the acidic property of the system, temperature programmed desorption (TPD) of NH_3 has been done. Toluene alkylation by benzyl chloride has been carried out for the evaluation of catalytic activity. The most active system is found to be mixed Al/Zr pillared montmorillonite.

The advent of pillared clays or a porous material holding inorganic pillars between silicate layers of clay, has attracted considerable interest due to its large surface area and thermal stability[1], molecular sieving ability[2] and applicability to potential shape selective catalysis[3]. According to the type of pillars, a homogenous distribution of micro pores can be obtained with pore openings varying from 4 - 20 A°. By varying the size of the pillar, or the spacing between the pillars, or both, one may adjust the pore size to suit a particular application. In particular pillared clay catalysts are widely used for several reactions including cracking of hydrocarbons[4], disproportionation of 1,2,4 - trimethylbenzene to yield tetramethylbenzene[5,6] , alkylation reactions and other similar routes which are catalysed by acid centres. The activity of pillared clays in bringing about the conversion and polymerisation of organic compounds under relatively mild conditions may be ascribed to the ability of pillared clays to donate protons and accept electrons from the adsorbed species. Rare earth oxides are effective catalysts for a number of reactions of industrial importance. However, there is not much report on the surface properties and catalytic activity of rare earth exchanged pillared clays.

In the present study, Na-montmorillonite is pillared with aluminium oxide, zirconium oxide and mixed aluminium and zirconium oxide clusters. Pillared clays are also prepared after exchanging Na+ ions with Ce, La, Sm - ions and then pillared with aluminium oxides. Pillared clays have both Brönsted and Lewis acid sites[7,8]. The Lewis acidity of pillared clays is comparable or even stronger than that of zeolite Y. Zr and Al pillared clays are active catalysts for methanol conversion to hydrocarbons. In this note we report the acid base property of Al, Zr - pillared, mixed Al/Zr pillared and Ce, Sm, La - exchanged Al pillared montmorillonite and it is correlated with the catalytic activity towards alkylation of toluene using benzyl chloride.

An important synthetic limitation of Friedel-Crafts alkylation is that rearrangement frequently takes place in the reagent. The classical catalysts used for this reaction are $AlCl_3$, $GaCl_3$, $FeCl_3$, $ZrCl_4$ etc. But these catalysts are highly corrosive and disposal of these used heterogeneous catalysts are highly problematic. In this context, acidic pillared clays offer a great promise. The alkylation products of toluene are important raw materials for the synthesis of a variety of pharmaceuticals and polymers. One of the important catalytic processes based on shape selectivity is the production of *p*-xylene by alkylation of toluene with methanol. Urabe and Izumi reported that the selectivity of Al pillared clays in this reaction is surprisingly higher than that of the zeolite ZSM-t[9]. Matsuda and Kikuchi claimed that the high selectivity of the pillared clays is a result of its moderate acidity resulting in a decrease in secondary isomerisation of the primary product[10]. The aim of the present investigation is to understand the selectivity and activity of Al/Zr pillared clays and their Ce, Sm, La-exchanged analogues.

Experimental

Catalyst preparation

The Na- montmorillonite used in this study was of commercial origin (Fluka, KSF) with surface area 15.42 m^2/g and bulk density 810 g/l and the composition is given in Table 1. It was used as such without purifica-

tion. The preparation procedure adopted was as reported by Figueras *et al.*[11]. The pillaring solution was prepared by the partial hydrolysis of 0 .1M Al(NO$_3$)$_3$ solution by 0.1M NaOH solution to obtain a series of a OH$^-$/ Al^{3+} ratio [OH$^-$/ Al^{3+}=1.75, 2, 2.25 and 2.5]. Without aging, the pillaring solution was then added drop wise to the previously prepared 1% slurry of montmorillonite to prepare aluminium pillared clay followed by filtration and calcination at 773 K. The Ce, Sm, La-exchanged aluminium pillared clays were also prepared with pillaring solutions of OH$^-$/Al^{3+} = 2 and 2.5 followed by washing, drying and calcination. Zirconium pillared clays were prepared by adding 800 ml of 0.4M ZrOCl$_2$ to 10 g of montmorillonite clay dropwise maintaining the temperature at 353 K followed by filtration and calcination at 573 K(ref. 6). The mixed Al/Zr pillared clays with OH$^-$/(Al+Zr) =1.75, 1.55 and 2.12 were also prepared.

Catalyst characterisation

For phase identification, powder XRD were obtained using Ni filtered Cu K$_\alpha$ radiation. Measurement of surface area of clay catalysts was done by nitrogen adsorption using BET method. Temperature programmed desorption (TPD) of ammonia was used to measure the acidity of pillared clay catalysts. This method is based on desorbing the ammonia adsorbed on the solid by heating at a programmed rate. The catalyst was first degassed by heating in a stream of nitrogen at 300°C. It is then cooled to room temperature and ammonia was adsorbed. The catalyst was then heated through a temperature programme in nitrogen flow. The ammonia desorbed in three different temperature regions (°C), 100-200, 200-400 and 400-600 is trapped in sulphuric acid and determined volumetrically and assigned as weak, medium and strong acid sites respectively.

Catalytic activity was determined by toluene alkylation reaction. 0.1g of the catalyst was added to 10.99 moles of toluene and 1 mole of benzyl chloride and refluxed in oil bath. The onset of the reaction was indicated by the evolution of HCl. After a particular time the reaction mixtures were taken and analysed using gas chromatography. The relative concentrations of components in the reaction mixture were calculated from the peak areas.

Results and discussion

The XRD values of the clay catalysts are listed in Table 2. Na-montmorillonite gave a characteristic peak

Table1- Elemental composition of the parent montmorillonite

Element	Weight%	Atomic%
Na	0.83	1.09
Mg	1.98	2.45
Al	17.94	19.97
Si	50.78	55.31
S	14.76	13.82
K	1.59	1.22
Ca	2.97	2.23

at $2\theta = 9.2$ indicating a $d(001)$ spacing of 9.6 A°. Ion exchange with poly hydroxy aluminium and zirconium cation replaces the hydrated cation bringing about an expansion in the basal spacing[12,13]. Aluminum pillared clays with different OH$^-$/Al^{3+} ratios, 1.75, 2, 2.25 and 2.5, gave basal spacings of 16.02, 17.66, 15.88 and 16.66 A° respectively. Thus maximum basal spacing , $d(001)$ is given by aluminium pillared clay (OH$^-$/Al^{3+} = 2). The small decrease in basal spacings of Ce, La, Sm -exchanged aluminium pillared clay may be due to the presence of Ce, La, Sm ions , the pillaring solution may be partially hydrolysed and the pillar may not have the Al$_{13}$ species. However, this observation is contradictory to that reported by McCauley[14] . But other scientists have got d spacings similar to Al pillared montmorillonite[15]. This controversy emphasizes the difficulty of comparing pillared clays obtained from different methods. The basal spacings, d (001) of mixed Al/Zr pillared clays at various OH$^-$/(Al + Zr) ratios i.e. 1.55, 1.75 and 2.12 were found to be 18.46A°, 17.35A° and 16.9 A° respectively. The basal spacing of zirconium pillared montmorillonite is found to be 17.15 A°.

It is well known that pillaring endows the clay material with greater surface area, acidity and micro porosity[11]. The surface area of various clay catalysts are also shown in the Table 2. Pillaring of Na-montmorillonite with pillaring agents of OH$^-$/Al^{3+}= 1.75, 2, 2.25 and 2.5 increase the surface area. But the increase in surface area is not up to the expected level, may be due to the following reasons.(i) The separation of larger particles from the parent Na montmorillonite was not done. (ii) The lack of aging of pillaring solution. For Ce, La, Sm -exchanged aluminium pillared clay the surface area is lower by around 25 units, may be due to the partial hydrolysis of pillaring solution. Zirconium pillared and

Table 2 - Surface characteristics and catalytic activity of different pillared clays

Catalyst	S.A (m²/g)	d(001) (A°)	Acidity (10⁻²mmol/g)			Catalytic activity µg s⁻¹m⁻²
			Weak	Medium	Strong	
[a]Na-mont	15.42	9.26	2.35	2.59	2.43	-----
[b]AlP 1.75	49.32	16.02	4.74	4.48	5.79	9.46
[b]AlP 2	70.32	17.66	3.29	6.57	7.23	18.85
[b]AlP 2.25	42.97	15.8	3.54	3.94	8.65	6.67
[b]AlP 2.5	59.99	16.66	3.27	4.46	4.98	9.13
[c]SmAlP 2	40.50	16.01	7.31	4.43	4.57	7.65
[d]LaAlP 2	42.24	15.83	6.73	4.68	4.46	6.95
[e]CeAlP 2	41.09	15.65	4.03	4.72	3.57	7.20
[c]SmAlP 2.5	42.04	15.23	4.72	5.53	5.16	9.65
[d]LaAlP 2.5	41.78	14.82	5.49	5.68	5.75	9.02
[e]CeAlP 2.5	40.39	14.24	3.46	5.43	4.07	9.13
[f]ZrP 0.4	94.48	17.15	5.47	7.06	4.43	19.28
[g]Zr/Al 1.55	98.97	18.46	4.76	7.89	4.42	20.12
[g]Zr/Al 1.75	92.02	17.35	4.88	7.26	4.98	18.8
[g]Zr/Al 2.12	89.42	16.90	4.37	7.53	4.87	16.90

[a] Na -montmorillonite

[b] Al pillared montmorillonite with OH⁻/ Al $^{3+}$ ratio = 1.75, 2, 2.25 & 2.5

[c] Sm exchanged Al pillared montmorillonite with OH⁻/ Al $^{3+}$ ratio = 2 & 2.5

[d] La exchanged Al pillared montmorillonite with OH⁻/ Al $^{3+}$ ratio = 2 & 2.5

[e] Ce exchanged Al pillared montmorillonite with OH⁻/ Al $^{3+}$ ratio = 2 & 2.5

[f] Zr pillared montmorillonite

[g] Mixed Zr/Al pillared montmorillonite with OH⁻/ Zr + Al ratio = 1.55,1.75 & 2.12

all the Al/Zr pillared montmorillonite showed an increase in surface area compared with Al pillared montmorillonite.

The acidity measurement was determined by temperature programmed desorption of ammonia. By comparing the acidities in weak, medium and strong regions with the catalytic activity, it is seen that the medium acidic region plays the major role in benzylation reaction. The results are given in Table 2. Na-montmorillonite has low acidity distributed almost equally in all the three regions. The difference in acidity between the aluminium pillared and the Ce, La, Sm-exchanged Al

pillared montmorillonite is associated with the initial sites of ion exchange, not occupied by the pillars which represents the 30% of the initial exchange capacity of the clay[11]. It is expected that Ce, La, Sm- exchanged Al pillared clay catalysts should possess more acidity compared with Al pillared clays. However, the acidity in Ce, La, Sm-exchanged Al pillared clays is comparatively less, probably due to the presence of Ce, La, Sm ions Al_{13}^{7+} undergoes hydrolysis and break the polymeric species. This is also seen as the lowered d(001) spacings in the XRD pattern of Ce, La, Sm-exchanged Al pillared clays. Zr pillared and mixed Zr /Al pillared

montmorillonite possess higher acidity compared to Al pillared clays , supported by the higher surface area and larger basal spacings.

Toluene alkylation with benzyl chloride was done on these acidic pillared clays. The G.C. analysis showed the selective formation of the single product irrespective of the catalyst used. The highest catalytic activity was found with mixed Zr/Al pillared clay with pillaring agent of $OH^-/(Al+Zr) = 1.55$. This could be explained by the higher surface area and surface acidity compared to other catalysts.

Acknowledgement

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