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# Ultrasonication: a competitive method of intercalation for the preparation of alumina pillared montmorillonite catalyst

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## Abstract

A  $\text{Ca}^{2+}$ -montmorillonite clay has been pillared with aluminium hydroxy polycations using ultrasonic technique. This pillared clay is compared with that obtained by conventional method of pillaring. XRD, FTIR in the framework region and surface area measurements elucidate that ultrasonically achieved pillaring is very homogeneous as compared to conventional technique. The uniform pillaring is responsible for the enhanced thermal and hydrothermal stability. However, the use of ultrasonics does not alter the inherent properties such as acidity of the pillared clays, as indicated by IR spectroscopy of adsorbed pyridine. The catalytic activities in the decomposition of propan-2-ol and cumene further confirms the strong acidity of the pillared clays, obtained either by ultrasonic or conventional techniques. In the time on stream studies for both the reactions, slower deactivation was observed on pillared clay prepared by ultrasonication route. Thus, the pillared clay can be obtained via., ultrasonication method of intercalation within 20 min at ambient temperature, with improved textural properties leading to higher stability of the material, without compromising on acidity or catalytic activity of the pillared clay. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:**  $\text{Ca}^{2+}$ -montmorillonite clay; Propan-2-ol; Zeolite Y

## 1. Introduction

Creating permanent microporosity with internal volume of  $0.5 \text{ ml g}^{-1}$ , yielding thermally stable material with surface area increment from 50 to  $300 \text{ m}^2 \text{ g}^{-1}$  and many fold enhancement in the acidity of a parent clay material, through a process called “pillaring” of clays is a vivid research area. This process comprises exchanging the charge balancing interlayer cations of the smectite clay with bulky, highly charged inorganic cationic polymeric species, followed by calcination. Upon heating, intercalated species transform into robust oxide particles as pillars, which props the

expanded layers of the clay. Considerable success has been achieved in the synthesis and characterization of the pillared clays and has been reviewed recently [1].

The most extensively studied and explored pillared material is the alumina pillared montmorillonite clay. The solution chemistry of  $\text{Al}^{3+}$  is well understood [2]. The structure of the polycation of  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$  consists of 12 octahedral Al, arranged in four groups of three octahedra around a central  $\text{AlO}_4$  tetrahedron [3]. Due to its high charge,  $\text{Al}_{13}$  easily replaces other existing interlayer cations in the clay. Upon dehydroxylation,  $\text{Al}_{13}$  is believed to get converted into  $\gamma\text{-Al}_2\text{O}_3$  type material [4]. The alumina pillared clays are stable in the redox atmosphere and offer acidic sites of the strength comparable to zeolite

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Y. Thus, alumina pillared clays are considered to be competent cracking catalysts [5].

However, from technological point of view, there are a number of issues remain to be explored. Firstly, a reliable and reproducible preparative procedure must be laid down. This is because the physico-chemical properties of these pillared materials may vary widely during various stages of the preparation. The aging of the polycations, drying and calcination of the intercalated clay are some of the critical steps which influence the porosity and acidity of the pillared derivatives [6]. Secondly, poor thermal and hydrothermal stability of these materials restricts their use in refinery applications. Upon applying high temperatures, the pillars start migrating and agglomerate. This leads to collapse of the pillared structure leaving behind a quasi-amorphous material with total loss of microporosity and surface area. Apparently, uniform distribution of the pillars within the clay layers seems to be the preliminary requirement for a stable pillared clay. Use of competitive exchange [7], reflux treatment to pillaring species prior to intercalation [8], the partial substitution of  $\text{Al}^{3+}$  by iso-electronic cations in  $\text{Al}_{13}$  [9] are some of the noteworthy attempts to improve the stability of the pillared clays. Recently, we have reported a novel method of intercalation, wherein  $\text{Al}_{13}$  can be introduced in-between the layers of  $\text{Ca}^{2+}$ -montmorillonite within 20 min and at ambient temperature. The entire process is simple and fast, and uniform pillaring is achieved due to accelerated diffusion of polycations through ultrasonics [10]. With the aim to investigate further, the cause and effect of this technique on the final properties of the pillared clay, this work is focused on the optimization of preparative conditions. The thermal and hydrothermal stability of the pillared clay prepared through ultrasonic technique is evaluated and its catalytic activity is compared with that of pillared clay prepared by conventional route.

## 2. Experimental

### 2.1. Materials

A commercial montmorillonite clay with chemical composition  $\text{SiO}_2$  69.1,  $\text{Al}_2\text{O}_3$  18.7,  $\text{Fe}_2\text{O}_3$  4.4,  $\text{TiO}_2$  0.37,  $\text{MgO}$  4.19,  $\text{CaO}$  2.93,  $\text{K}_2\text{O}$  0.25, and  $\text{Na}_2\text{O}$

0.07 wt% was used during the study. The coarse particles were removed by sedimentation technique prior to use as host material for pillaring. The cation exchange capacity determined was  $0.75 \text{ meq g}^{-1}$  with surface area of  $78 \text{ m}^2 \text{ g}^{-1}$  consisting of broad range of pore size. An oriented film of this clay showed no impurities of quartz or mica in the powder X-ray diffraction profile. The hydroxy aluminium oligomer used was procured from Rehies Chemical, USA, under the trade name of Chlorhydrol.

### 2.2. Preparation of pillared clay

An aqueous solution of Chlorhydrol was mixed with 5% clay suspension in water so as to provide 10, 20, 30 and 60 meq of  $\text{Al}^{3+} \text{ g}^{-1}$  of clay. The mixture was immediately kept in the ultrasonic bath (Sheshin, Japan, operating frequency 50 KHz) at ambient temperature (300 K) for varied duration viz., 10, 20, 40 and 60 min. The product was filtered, washed with water till the filtrate was free from chloride ions ( $\text{AgNO}_3$  test) and dried at room temperature under vacuum. The intercalated material was heated to 773 K in a programmable furnace at  $10 \text{ K min}^{-1}$  and further calcined for 6 h. The sample obtained after optimizing the Al concentration and ultrasonication period, for the simplicity, was designated as PILCUS. For comparison, a pillared clay sample was also prepared by conventional method. The pillaring species was added dropwise to the clay suspension as the intercalation reaction was carried out at 353 K for 6 h under vigorous stirring. The sample was given the same after-treatment and designated as PILCCONV.

### 2.3. Characterization

X-ray diffraction patterns of the powdered samples were recorded on Rigaku D Max III VC machine, using Ni-filtered  $\text{Cu K}\alpha$  radiation. Chemical composition of the samples was analysed by X-ray fluorescence technique on Rigaku 3070 X-ray wavelength dispersive spectrometer. BET equation was used to obtain the surface area from the nitrogen adsorption isotherms done on Omnisorp 100 CX (Coulter) instrument. The samples were degassed at 523 K for 6 h. The relative pressure  $p/p_0$  was in the range of 0.001–0.1. Horwath–kawazoe model was applied to get

effective pore diameter. The micropore volume was estimated using the *t*-plot.

$^{27}\text{Al}$  NMR spectra of the pillaring species were taken on MSL 300 NMR spectrometer, using a conventional 10 mm high resolution probe. The samples were taken in 10 mm OD nmr tubes and a capillary containing  $\text{D}_2\text{O}$  was used for the field-frequency locking.  $^{27}\text{Al}$  NMR for the solid samples were recorded on the same instrument at 78.2 MHz. The samples were packed in a 7 mm OD zirconia rotor and spun at 2.5–3.1 KHz. The spectral width was 125 KHz, pulse width of 1  $\mu\text{s}$ , and the relaxation delay was 500 ms. 3000 scans were accumulated and the data were collected using conventional “CYCLOPS” sequence. The chemical shifts are referred to 1 M aqueous solution of  $\text{Al}(\text{NO}_3)_3$ .

The framework IR spectra (1300–400  $\text{cm}^{-1}$ ) and chemisorbed pyridine were recorded using Nicolet 60 SXB spectrometer, with 4  $\text{cm}^{-1}$  resolution, acquiring over 500 scans. The sample was pressed into a self-supporting wafers (5–6  $\text{mg cm}^{-2}$ ) and placed in the transmittance cell. It was then evacuated to  $10^{-6}$  torr while heating to 673 K at a rate of 5  $\text{K min}^{-1}$ , and kept at 673 K for 3 h. It was then cooled down to 373 K and the spectrum was recorded. The sample was then equilibrated with pyridine vapours at 10 mm partial pressure for 30 min. The excess of pyridine was pumped off and the spectrum was recorded. The sample was then evacuated at 473, 573 and 673 K and spectra were recorded.

## 2.4. Catalytic tests

The samples were pelletized and sieved to 10 mesh size and loaded in a fixed bed down flow tubular quartz reactor of 10 mm diameter. The samples were activated at 673 K for 3 h under dry  $\text{N}_2$  stream (30  $\text{ml min}^{-1}$ ) and then cooled down to desired reaction temperatures.

### 2.4.1. The decomposition of cumene

The reaction was carried out at 573 K for lower conversion. The undiluted cumene was passed over the catalyst bed at two different WHSVs viz., 2.6 and  $5.2 \text{ h}^{-1}$ . The products were identified on GC–MS after condensation in a cold trap, and analysed rou-

tinely after every 30 min using a gas chromatograph equipped with a 50 m long methyl–silicon gum capillary column and a flame ionization detector.

### 2.4.2. The decomposition of propan-2-ol

The reaction was carried out at 473 K for 3 h. Vapours of propan-2-ol were passed over the catalyst at a WHSV of  $3.1 \text{ h}^{-1}$ . The products were analysed after every 30 min using a gas chromatograph equipped with both TCD and FID detectors and a 2 m long and 3 mm diameter poropak “Q” column.

## 3. Results and discussion

### 3.1. Optimization of ultrasonic treatment

As evident from Table 1, two factors that influence the quality and extent of pillaring are the duration of ultrasonication and the concentration of  $\text{Al}_{13}$ . At lower duration ca. 10 min, not much of  $\text{Al}_{13}$  are diffused inside the clay, which is confirmed by lower  $\text{Al}_2\text{O}_3$  incorporation, the surface area and pore volume. On the other hand, after 60 min, more  $\text{Al}_2\text{O}_3$  is fixed due to the delamination of clay layers. The X-ray profile of such a sample showed no reflections corresponding to (0 0 1) plane and the delaminated clays are known to possess meso and macroporosity with negligible or very low microporosity [11].

The ultrasonic treatment for 20 min yielded very sharp and intense peaks in the X-ray pattern, suggesting the uniformity of pillaring. The surface area and micropore volume of this sample were also optimum. When the pillaring was carried out, keeping 20 min of ultrasonic treatment as constant and by varying the concentration of  $\text{Al}^{3+}$ , optimum results were obtained for the sample with  $\text{Al}^{3+}$  to clay ratio of 20  $\text{meq g}^{-1}$ . At lower concentrations, pillaring species hydrolyse, thereby leading to more  $\text{Al}^{3+}$  fixation rather than  $\text{Al}_{13}$ . In the highly concentrated solution,  $\text{Al}_{13}$  further polymerizes and the diffusion of such species is limited [12]. The sample prepared by treating 20  $\text{meq}$  of  $\text{Al}^{3+} \text{ g}^{-1}$  clay for 20 min of ultrasonication, is designated as PILCUS. For comparison, the values of conventionally prepared pillared clay are also presented in Table 1.

Table 1  
Effect of ultrasonic duration and Al to clay ratio on the pillared clay materials

Time (min)	meq Al <sup>3+</sup> g <sup>-1</sup> clay	<i>d</i> <sub>0 0 1</sub> (nm)	Al <sub>2</sub> O <sub>3</sub> incorporated mass (%)	<i>S</i> <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	<i>V</i> <sub>μ</sub> (ml g <sup>-1</sup> )
10	20	1.83	14.42	119	0.04
20 [PILCUS]	20	1.92	16.47	281	0.11
40	20	1.83	19.18	212	0.08
60	20	–	23.66	265	0.05
20	10	1.89	17.88	170	0.06
20	30	1.87	13.55	233	0.08
20	40	1.86	10.35	226	0.08
PILCCONV	20	1.81	15.14	175	0.07

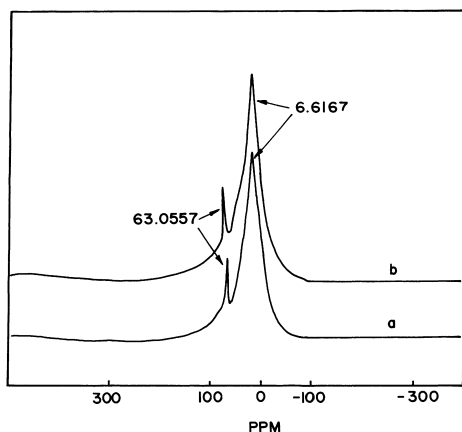


Fig. 1. <sup>27</sup>Al NMR spectra of aqueous solution of Chlorhydrol (a) before and (b) after 20 min of ultrasonication.

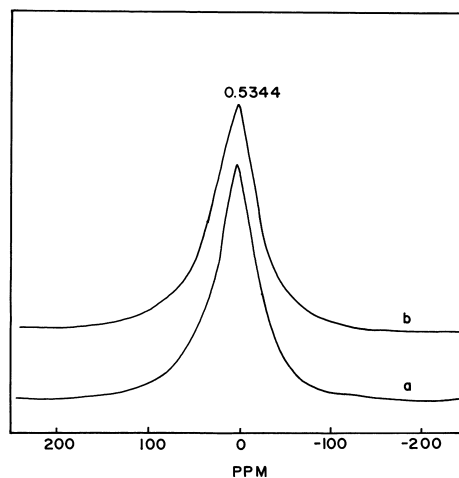


Fig. 2. <sup>27</sup>Al MAS NMR spectra of parent clay material (a) before and (b) after 20 min of ultrasonication.

### 3.2. NMR studies

Effect of ultrasonics on the Al<sub>13</sub> was examined by <sup>27</sup>Al liquid NMR spectroscopy. A sharp signal at 63 ppm corresponds to tetrahedrally coordinated Al, whereas a broad peak around 0 ppm confirms Al in the octahedral environment. The broadening of octahedral signal is probably due to electric field gradient effect [4]. When the spectra were recorded before and after 20 min of ultrasonic treatment, we observed no change in the chemical shifts, as shown in Fig. 1, suggesting that ultrasonics does not affect the nature and structure of pillaring species.

Similarly, MAS NMR spectrum of the parent clay shows that all the Al is in the octahedral environment (Fig. 2.) When the clay was treated ultrasonically for 20 min, no change in the NMR signal was observed.

### 3.3. Stability of pillared materials

To evaluate the thermal stability of the pillared clays, both PILCUS and PILCCONV were calcined at different temperatures for 6 h. The change in “*d*” spacing and surface properties are presented in Table 2.

The main change observed above 773 K is the gradual decrease in the “*d*” value. The 0 0 1 peak disappears above 973 K for PILCCONV sample, suggesting the structural collapse. However, in the case of PILCUS, as can be seen from the table, the material is quite stable with marginal decrease in the surface area and microporosity. Even at 1173 K, PILCUS sample exhibits better textural properties than PILCCONV. The observable (0 6 0) reflection in the X-ray profile of PILCUS sample shows that the lamellar structure of the clay is still preserved at 1173 K. Similar results

Table 2  
Effect of thermal treatment on the pillared clays

Temperature (K)	PILCUS				PILCCONV			
	$d_{0.01}$ (nm)	$S_{BET}$ ( $m^2 g^{-1}$ )	$V_{\mu}$ ( $ml g^{-1}$ )	Mesopore area ( $m^2 g^{-1}$ )	$d_{0.01}$ (nm)	$S_{BET}$ ( $m^2 g^{-1}$ )	$V_{\mu}$ ( $ml g^{-1}$ )	Mesopore area ( $m^2 g^{-1}$ )
773	1.92	281	0.11	21	1.81	175	0.06	11.5
973	1.83	237	0.09	7	1.80	48	0.02	1.2
1173	1.76	61	0.02	5	–	<10	–	–
1023 <sup>a</sup>	1.81	189	0.065	22	–	15	0.004	4.9

<sup>a</sup>100% steam, 8 h.

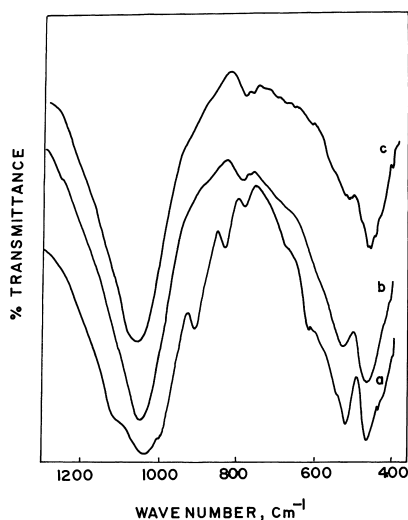


Fig. 3. Framework infrared spectra of (a) parent clay, (b) PILCCONV and (c) PILCUS.

were observed when the steaming treatment was given according to ASTM procedure, for both the samples. The higher stability of PILCUS can be explained on the basis of uniform pillaring.

### 3.4. IR spectra in the framework region

In the framework FTIR spectrum of the parent clay (Fig. 3(a)), the vibrational modes corresponding to Al–OH–Al and Al–OH–Mg bonding are observed at 913 and 844  $cm^{-1}$ , respectively.

It is known that the pillars will be anchored and that its bonding causes the rupture of Al–OH–Mg bond [4]. In the case of PILCCONV, (Fig. 3(b)), the band at

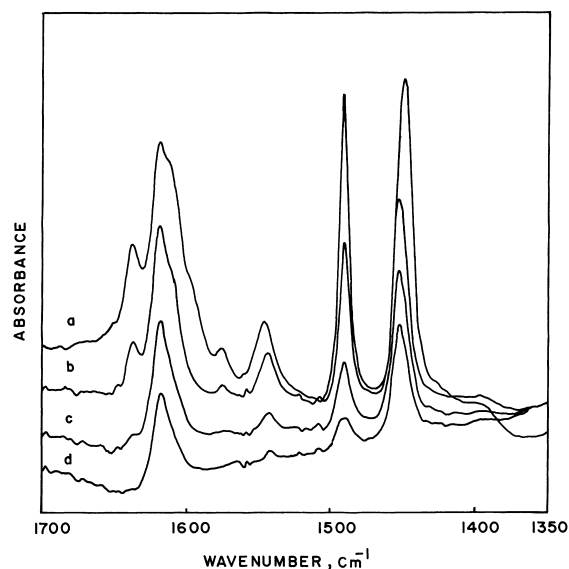


Fig. 4. Infrared spectra of pyridine adsorbed on PILCUS at (a) 373, (b) 473, (c) 573 and (d) 673 K.

844  $cm^{-1}$  appears as a shoulder, suggesting that the pillaring is not very uniform.

On the other hand, in PILCUS, Al–OH–Mg band is not observed (Fig. 3(c)), confirming that very uniform pillaring was achieved due to ultrasonication.

### 3.5. Surface acidity

Both PILCUS and PILCCONV show the presence of strong Lewis and Bronsted acid sites [13] as shown in the Figs. 4 and 5, respectively. The bands at 1450 and 1620  $cm^{-1}$  are due to coordinated pyridine via., its nitrogen loan-pair electrons to an empty p-orbital. Surface protons form pyridinium ion which gives rise to the band at 1547  $cm^{-1}$  and a very strong absorption

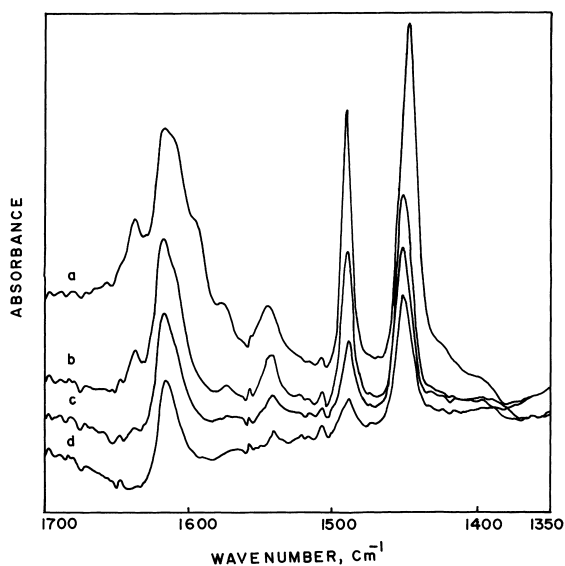


Fig. 5. Infrared spectra of pyridine adsorbed on PILCCONV at (a) 373, (b) 473, (c) 573 and (d) 673 K.

band at  $1490\text{ cm}^{-1}$ , indicative of  $\text{N}^+\text{-H}$  bonding. A band, around  $1492\text{ cm}^{-1}$ , indicates the presence of both Lewis and Bronsted acidity.

Upon heating the samples above 473 K, the band at  $1577\text{ cm}^{-1}$  due to physisorbed pyridine disappeared. From Figs. 4 and 5, it can be seen that pyridine desorption above 673 K resulted in preferential removal of pyridine bound to Bronsted acid sites relative to Lewis acid sites. The intense Lewis bands suggest that above 673 K, the surface has only Lewis type of acid sites. The relative acid site strengths were obtained at increasing desorption temperatures for both the samples, by considering the area under Bronsted ( $1550\text{ cm}^{-1}$ ) or Lewis peaks ( $1450\text{ cm}^{-1}$ ), as shown in Table 3.

Table 3  
Semiquantitative estimation of the acidity of pillared clays from IR spectroscopy

Temperature <sup>a</sup> (K)	PILCUS			PILCCONV		
	B	L	B/L	B	L	B/L
373	6.04	8.30	0.73	7.21	10.06	0.72
473	3.86	5.32	0.72	4.81	6.44	0.75
573	3.29	4.99	0.66	4.01	5.78	0.69
673	1.51	4.22	0.36	1.88	4.94	0.38

<sup>a</sup>The temperature of evacuation of adsorbed pyridine.

B is the area under the peak of Bronsted acid sites ( $1550\text{ cm}^{-1}$ ) after correction and L is the area under the peak of Lewis acid sites ( $1450\text{ cm}^{-1}$ ).

The comparable values of acid strength for PILCUS and PILCCONV suggest that there is not much of difference in the acidity of the two samples.

### 3.6. Catalytic studies

#### 3.6.1. Catalytic decomposition of cumene

It is known that for cracking activity, the catalyst should possess strong acid sites [14]. We observed benzene,  $\alpha$ -methyl styrene as major and p-cymene as major side product. The results are summarized in Table 4. In both the catalysts,  $\alpha$ -methyl styrene ( $\alpha$ MS) formed because dehydrogenation reaction is favoured. At lower WHSV, the substrate is in contact with the catalyst for longer time, and more side products are observed. At lower contact period, less side reaction has occurred, as observed on both the catalysts. The dealkylation product, benzene, is indicative of the presence of strong and a large number of Bronsted acid sites.

The benzene formation can take place in two ways. The first is the protonation of aromatic ring followed by the cleavage of chain-ring bond [15]. According to a second mechanism, dehydrogenation to  $\alpha$ MS, followed by protonation over Bronsted sites and subsequent rearrangement and/or cleavage, can occur [16]. The second path leads to other side chain-cracked products. Since both catalysts give more of  $\alpha$ MS along with side products, apparently, the second mechanism holds good for the system.

#### 3.6.2. Catalytic decomposition of propan-2-ol

The reaction prominently yielded propene, a dehydration product, as compared to dehydrogenation product, acetone at 473 K, on both the catalysts.

Table 4  
Catalytic decomposition of cumene on pillared clays

Catalyst	WHSV (h <sup>-1</sup> )	Time (h)	Cumeneconv. (wt%)	Selectivity (wt %)			Dealkylation/ dehydrogenation product ratio
				Benzene	$\alpha$ MS	$\Sigma$ SCC	
PILCUS	2.6	1	35.8	33.0	46.0	21.0	0.72
		2	32.0	29.0	54.0	17.0	0.54
		3	30.1	17.1	65.6	17.3	0.29
		4	29.6	15.3	79.5	5.1	0.19
	5.2	1	22.0	35.8	57.2	7.0	0.62
		2	18.2	30.1	64.1	5.8	0.47
		3	14.9	27.1	68.0	4.9	0.40
		4	9.14	23.3	71.0	4.7	0.32
PILCCONV	2.6	1	32.2	27.0	50.0	23.0	0.54
		2	28.9	24.3	59.3	16.4	0.41
		3	26.8	22.0	65.0	13.0	0.34
		4	24.5	10.3	72.0	17.7	0.14
	5.2	1	21.6	35	51.0	14.0	0.69
		2	16.4	25.8	61.2	13.0	0.42
		3	12.5	15.3	71.8	12.94	0.21
		4	8.75	12.9	75.0	12.1	0.17

Reaction temperature: 573 K.

$\Sigma$ SCC is the summation of side chain cracked products.

Table 5  
Catalytic decomposition of propan-2-ol on pillared clays

Catalyst	Time (h)	Propan-2-ol Conv. (wt%)	Selectivity (wt%)	
			Propene	Acetone
PILCUS	1	99.0	98.1	1.9
	2	98.3	98.1	1.9
	3	96.4	98.1	1.9
PILCCONV	1	99.0	97.9	2.1
	2	95.1	97.7	2.3
	3	93.6	97.4	2.6

Reaction temperature=473 K, WHSV=3.132 h<sup>-1</sup>.

However, we observed no ether formation, on any of the catalysts. Table 5 compares the time on stream studies for the catalytic activities. The selective formation of propene suggests that both the catalysts have high surface acidity [17], thus confirming the IR results. The steady decrease in the conversion level suggests that propene is strongly adsorbed on the catalyst surface.

In the case of cumene cracking reaction, the deactivation of the catalysts may be due to strong adsorption of aromatic compounds or propene. Here, in the

case of pillared clays, propene seems to be responsible for the observed deactivation, as further supported by the propan-2-ol decomposition reaction. In both catalysts, the extent of deactivation (as observed by the decrease in the conversion) is less in the case of PILCUS, as compared to PILCCONV.

#### 4. Conclusions

An alternative method of intercalation, employing ultrasonics, provides a faster and effective mode of pillaring of clay with alumina. As compared to lengthy procedures of conventional techniques, the process is time effective and easy to scale-up. A higher surface area from homogeneously distributed, well-defined pores provides better access to reactant molecules. The microporous network is comparatively more stable towards thermal treatment and can even sustain in the presence of steam. However, the catalytic tests elucidate that the catalysts deactivate significantly. In the case of pillared clay, intercalated through ultrasonication, the observed rate of deactivation is less. However, the employment of ultrasonics does not alter the inherent properties like the acidity and the cata-

lytic activity of the pillared clay. Since ultrasonic treatment does not affect the structure of the host or guest moiety, this method can be easily extended to achieve intercalation of any layered material with the pillars of interest.

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