

# Preparation, characterization and catalytic activity of titania pillared montmorillonite clays

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## Abstract

Titania pillared clays are prepared through a novel method using titania sol via colloidal route as the pillaring agent. Formation of pillared clay (PILC) is proved from the physico-chemical characterization using X-ray diffraction (XRD), surface area–pore volume measurements, thermogravimetric analysis (TGA), infrared (FTIR) spectroscopy and elemental analysis (ICP-AES). The acidity of the catalysts is measured from temperature-programmed desorption (TPD) of ammonia. Ethylation of benzene with ethanol is carried out in gas phase to test the catalytic activity. Good correlation is obtained with alkylation activity and acidity. Enhanced porosity upon pillaring allows shape selective catalysis within the pores to get ethylbenzene as the only product.

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## 1. Introduction

Pillared clays (PILCs) are two-dimensional zeolite-like materials prepared by exchanging charge compensating cations between the clay layers with large inorganic metal hydroxycations, which are oligomeric and are formed by hydrolysis of metal oxides or salts [1]. After calcination, the metal hydroxy cations are decomposed into oxide pillars that keep the clay layers apart and create interlayer and interpillar spaces, thereby exposing the internal surfaces of the clay layers. Baes and Meisner, Burch, etc. had reported that, in principle, any metal oxide or salt that forms polynuclear species upon hydrolysis can be inserted as a pillar [1–5].

Compared to other porous solids, pillared clays demonstrate their advantage in several aspects. First, clays are abundant material and pillared clays are generally synthesized under moderate conditions with much simple procedures compared to zeolite synthesis [6,7]. Another feature is that some pillared clays have pore openings of about

1 nm or even larger [6], being much larger than those in zeolites (0.3–0.7 nm) [7]. So PILCs have a potential to serve as molecular sieves and shape selective catalysts for a wide range of molecular sizes. Furthermore, multiple components like transition metals and rare earth elements can be readily introduced into PILCs by intercalating clays with mixed pillars of oxides [5,8,9].

Ti-PILC has a considerably larger interlayer spacing in comparison with other metal oxide PILCs and shows high adsorption ability [10–17]. Thus, titania pillars are very useful in designing shape selective catalysts. In general, two different methods to create Ti complexes suitable for pillaring processes were reported in the literature. The first method to form Ti complexes in solution is the addition of  $\text{TiCl}_4$  to 5 or 6 M HCl followed by dilution with distilled water and ageing from 3 h up to as long as 20 days prior to their use as pillaring agents [12,18,19]. Drawbacks of this preparation route are the highly acidic conditions one has to work in, resulting in leaching of Al and Si from the clay structure [13,19] and the requirement of careful handling of the  $\text{TiCl}_4$ . The second route is based on the hydrolysis of various Ti alkoxides under much milder acidic conditions [20–25]. Both these precursors should be carefully treated

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during sol preparation to avoid prior hydrolysis by moisture that lead to the hydroxide formation. XRD patterns of some Ti-PILCs [26,25] show a relatively large amount of unexpanded clay. This portion may consist of either unreacted clay or clay exchanged with some types of monomeric Ti species. Valverde et al. [27] reported that there are two  $2\theta$  values corresponding to the (100) plane due to different pillar species present. Another drawback of titania pillaring precursors is their high cost and difficulty in laboratory preparation from raw titania. Other metal PILCs mainly use inorganic salt precursors for pillaring agent preparation [28–33] and up to now there are no reports on Ti-PILCs that use inorganic salt precursors other than  $\text{TiCl}_4$ . Thus, the use of other inorganic precursors in pillaring agent preparation is promising.

The main aim of the present work is to prepare Ti-PILC via a cheap route, compared to the existing methods; using a cheap precursor and mild conditions. The precursor used for the preparation of the pillaring solution is the cheaply available titanyl sulphate,  $\text{TiOSO}_4$ . This precursor is found to be stable in air and moisture which allows rough handling. PILCs with different physico-chemical properties have been prepared by using ultrasonic techniques [34] and microwave conditions [35]. Here we report a simple, easy methodology for Ti-PILCs, suitable for shape selective organic transformations.

The catalytic activity of the pillared clay is evaluated for ethylation of benzene to give ethylbenzene, the important raw material in the petrochemical industry for the manufacture of styrene, which is a widely used industrial monomer. Worldwide capacity of ethylbenzene production is about 23 million metric tons per year [36]. Conventionally ethylbenzene is produced by benzene alkylation with ethylene using homogeneous mineral acids such as aluminium chloride or phosphoric acid as catalysts that cause a number of problems concerning handling, safety, corrosion and waste disposal. Society now demands alternative eco-friendly catalysts, which make clays, zeolites, and other solid acid catalysts important. Clay-based catalysts have been extensively studied for alkylation of hydrocarbons [34,35,37–40]. The present work makes use of ethanol and benzene for the selective formation of ethylbenzene on titania pillared montmorillonite.

## 2. Experimental

### 2.1. Materials

Pillaring is done on montmorillonite KSF (Aldrich). Prior to pillaring, KSF is treated with 0.5 M sodium nitrate (Merck) solution at 70 °C for 24 h, then filtered, made nitrate free by washing and is dried at 110 °C to get the sodium-exchanged montmorillonite. Treatment with sodium nitrate replaces the exchangeable cations  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{H}^+$ , etc. present between the layers i.e. when the mineral is immersed in an electrolyte, exchanges governed by the principle of equivalence will take place

between the external and internal cations. Titania pillaring agent is prepared using the method reported by Sivakumar et al. [41]. Titanyl sulphate (M/s Travancore Titanium Products, Trivandrum, India, 99% purity) is used as a precursor for the synthesis of titania sol. In a typical experiment, titanyl sulphate is dissolved in 500 ml of distilled water (0.2 M) and is hydrolyzed by slow addition of ammonium hydroxide (10%, S.D Fine Chemicals Ltd.) solution under constant stirring at room temperature, until the reaction mixture attained a pH of 7.5. The precipitate obtained is separated by filtration and is washed free of sulphate ions with distilled water. The precipitate is further dispersed in 1 l of hot distilled water and is peptized by the addition of 10%  $\text{HNO}_3$  (Merck) solution to get titania sol at around a pH of 1.6. This pillaring solution is then added to the previously swelled 1% suspension of sodium-exchanged montmorillonite clay in distilled water, with a metal to clay ratio of 10 mmol/g. The solution is stirred at 70 °C for 24 h, kept overnight, filtered, washed free of nitrate ions, dried at 110 °C and calcined at 500 °C for 5 h to get titania pillared montmorillonite. Montmorillonite KSF is designated as M; sodium exchanged one as NM and titania pillared clay as TM. For comparison of physico-chemical properties and catalytic activity studies, both M and NM are also calcined at 500 °C for 5 h.

The pillaring solution precursor can be prepared by dissolving partially hydrated titania or metatitanic acid  $\text{TiO}(\text{OH})_2$  (M/s Travancore Titanium Products, Trivandrum, India, 98% purity) in hot concentrated  $\text{H}_2\text{SO}_4$  (Merck). It is then diluted and filtered to get the yellowish titanyl sulphate,  $\text{TiOSO}_4$  (0.2 M).

### 2.2. Characterization techniques

The X-ray diffraction pattern of the catalysts is obtained using a Rigaku D MAX III VC Ni-filtered Cu K alpha radiation ( $\lambda = 1.5404 \text{ \AA}$  at a scan rate of 4°/min). A Micromeritics Gemini 2360 surface area analyzer is used to get the BET surface area with  $\text{N}_2$  adsorption at liquid  $\text{N}_2$  temperature (77 K). The catalysts are heated at 400 °C for 3 h under a flow of nitrogen before running the analysis. The *t*-method of de Boer et al. [42] is used to calculate the micropore volume and external surface area of the catalysts. The difference between the BET surface area and the external surface area gives internal surface area, i.e., the surface area from pores. Mesopore volume is obtained by subtracting micropore volume from the total pore volume. The mean pore width is obtained from the relation  $d_m = 2V/A$ , where  $V$  is the pore volume and  $A$  is the internal surface area [43]. Elemental analysis of prepared catalysts is done with inductively coupled plasma-atomic emission spectrometer after the quantitative separation of silica using HF. Analysis is done using 'GBC' Plasmalab 8440M instrument. TG analysis of the dried samples is performed in a Perkin–Elmer Pyris Diamond thermogravimetric/differential thermal analyzer by heating the sample at a rate of 20 °C  $\text{min}^{-1}$  from room temperature

to 800 °C in air. To determine the acidity of the catalysts, ammonia TPD measurements in the range 100–600 °C were performed in a conventional flow-type apparatus at a heating rate of 20 °C min<sup>-1</sup> and in a nitrogen atmosphere [44]. Ammonia desorbed between 100 °C and 200 °C corresponds to weak acidity, those between 200 °C and 400 °C to medium strength, and above 400 °C is associated with strong acidity. FTIR spectra are obtained by the KBr pellet method on ABB BOMEM (MB Series) spectrometer in the range 400–4000 cm<sup>-1</sup>. Solid-state NMR experiments were carried out over a *Brucker DSX-300* spectrometer at resonance frequencies of 78.19 MHz for <sup>27</sup>Al and 59.63 MHz for <sup>29</sup>Si. XWINNMR software operating in a Unix environment in a silicon graphic computer was employed to acquire and retrieve the data. For all the experiments, a standard 4 mm double-bearing *Brucker MAS* probe was used. The chemical shifts were referred to external standards, viz. tetramethylsilane (TMS) for <sup>29</sup>Si studies at 0 ppm. Aluminium nitrate solution (0.1 M) was used as the external standard in the case of <sup>27</sup>Al.

### 2.3. Catalytic reaction

Benzene (Qualigens) and ethanol (Merck) are used as received. The catalyst was activated at 500 °C for 2 h before subjecting to the reaction. Benzene ethylation is carried out at atmospheric pressure in a fixed bed, vertical, down-flow glass reactor placed inside a double-zone furnace. Exactly 0.5 g of the sample is sandwiched between the layers of inert silica beads. A thermocouple detector monitors the temperature of the catalyst. The reactant is fed into the reactor by means of a syringe pump (Cole palmer®) at required WHSV, benzene to ethanol molar ratio and temperature. The products and the unreacted reactants are condensed by means of a water condenser, collected in an ice trap and liquid samples are subjected to gas chromatographic analysis using Chemito GC 1000 gas chromatograph with BP1 capillary column connected to a FID detector. The ethanol conversion and product selectivity (weight percentage) are noted.

## 3. Results and discussion

The present study introduces titania sol prepared from titanyl sulphate as the pillaring agent. The acidity of the sol is low compared to the TiCl<sub>4</sub> method, which decreases the dealumination and leaching of silicon. This route is very cheap compared to the existing methods for Ti-PILC preparation; only aqueous medium is required for pillaring agent preparation. The time used for sol preparation is less and no further aging of the sol is required as in the alkoxide route. Generally, pillaring solution is added to the swelled clay. But when the present pillaring solution is added to previously swelled parent montmorillonite KSF suspension, immediate gelation occurs to the sol. Sodium exchange of the parent montmorillonite is done and surprisingly on Na<sup>+</sup> exchange, montmorillonite suspension

stabilizes titania sol and prevents gelation. The reason may be the replacement of H<sup>+</sup> ions between the layers (since montmorillonite KSF is an acid treated clay), in addition to the exchangeable metal cations present. H<sup>+</sup> ions may change the pH of sol making the sol unstable in KSF.

### 3.1. XRD patterns and surface area–pore volume measurements

The X-ray diffraction (XRD) pattern of the parent, ion exchanged and Ti pillared clays is shown in Fig. 1. The XRD pattern of the parent and sodium-exchanged clays calcined at 500 °C exhibits a peak at ~9°, commonly assigned to the basal (001) reflection (*d*<sub>100</sub> is 9.8 Å) [28,43]. The shift in 2θ value (of (100) plane) and thus the increase in *d*-spacing upon pillaring are evident from Fig. 1. Klopogge [45] reported that pillared smectites are clays with high permanent porosity obtained by separating the clay sheets by a molecular prop or pillaring agent. Thus, the enhanced porosity and surface area shown in Table 1 are the result of the introduction of titania pillar. Sodium exchange also increases surface area and pore volume, which may be due to delamination and dealumination occurring during ion exchange. The *d*-spacing of the Ti-PILC calcined at 500 °C is 23.0 Å. Thus, Ti pillaring is found to be very effective for the development of thermally stable porous structure in clays. Yamanaka et al. reported that TiO<sub>2</sub> pillared montmorillonite gave a basal spacing at 23.2 Å at room temperature. The basal spacing of the sample is shifted to 22.2 Å when calcined at 500 °C [16]. The Ti-PILCs prepared in the present work did not show any unexpanded clay layers. The pillar solution contains same oligomeric species and thus only one peak corresponding to (100) plane is detected.

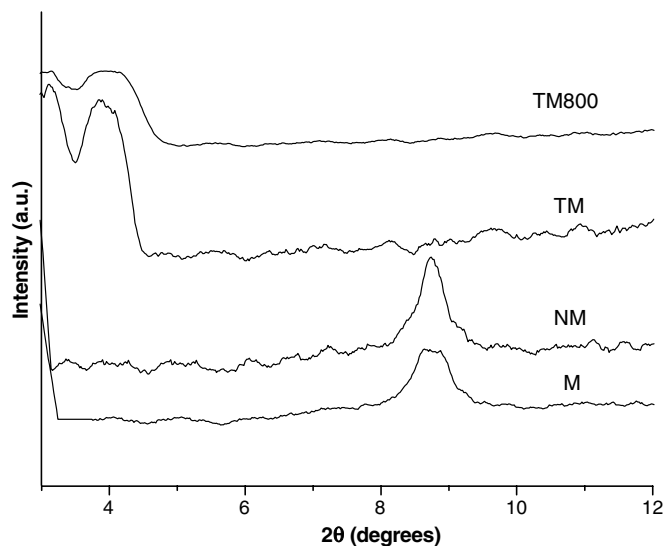


Fig. 1. X-ray diffraction pattern of parent, sodium ion exchanged as well as pillared montmorillonite.

Table 1  
Surface area–pore volume measurements and *d*-spacing of the various systems

Catalyst	TM	NM	M
BET surface area (m <sup>2</sup> /g)	132.84	51.64	7.90
External surface area (m <sup>2</sup> /g)	27.00	22.05	–
Internal surface area (m <sup>2</sup> /g)	105.84	29.59	–
Total pore volume (×10 <sup>-6</sup> m <sup>3</sup> /g)	0.1235	0.0512	0.0116
Micropore volume (×10 <sup>-6</sup> m <sup>3</sup> /g)	0.0660	0.0280	–
Mesopore volume (×10 <sup>-6</sup> m <sup>3</sup> /g)	0.0575	0.0232	–
Mean pore size (Å)	23.3	3.5	–
<i>d</i> -spacing (Å)	23.0	9.8	9.8
<sup>27</sup> Al NMR Al <sup>IV</sup>	0.28	1.70	–0.83
Al <sup>VI</sup> (δ ppm)	52.29	53.53	60.00
<sup>29</sup> Si NMR T(3Si, 1Al) (δ ppm)	–96.12	–94.80	–95.56

### 3.2. Elemental analysis

Table 2 gives the elemental analysis results of various systems, silica is separated first and the remaining elements are estimated using ICP-AES. The Si/Al ratio of parent montmorillonite is 3.18. On pillaring, the ratio is increased due to the leaching out of Al. Sodium content is increased after ion exchange at the expense of other exchangeable cations K<sup>+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>, etc. The decrease in the amount of exchangeable metal cations upon pillaring is clearly seen. Thus, the entrance of pillar metal replaces exchangeable cations. The enhanced porosity, which is evident from the increased interlayer distance, is the result of the pillar metal present.

### 3.3. FTIR analysis

Fig. 2 shows the FTIR spectra of the parent, ion exchanged and pillared montmorillonites. The two bands around 3500 cm<sup>-1</sup>, in the –OH stretching region are attributed to silanol groups (3740 cm<sup>-1</sup>) of the external layer and a broader band due to Al<sub>2</sub>OH group (3650 cm<sup>-1</sup>) of the octahedral layer [46]. Stretching vibrations of water molecules may also contribute to –OH peaks (3500 cm<sup>-1</sup>). On pillaring, the band broadens due to the introduction of more –OH groups of the pillar, which is interpreted as an effect of pillaring [44]. The decrease in intensity arises from the dehydration and dehydroxylation steps during pillaring. Peak at around 1600 cm<sup>-1</sup> is due to bending vibrations of water. Pillaring process replaces a large amount of interlayer cations that generally exist as hydrated and it decreases the intensity of –OH peaks. PILCs have low amount of adsorbed/coordinated water due to the

Table 2  
Elemental composition of various catalyst systems

Catalyst	Element (%)								
	Na	Mg	Al	Si	K	Ca	Fe	Ti	Si/Al
M	2.18	2.81	17.74	56.47	4.11	5.01	11.67	–	3.18
NM	5.56	2.69	15.52	58.85	3.80	2.08	11.50	–	3.79
TM	2.76	2.23	14.72	57.42	2.47	1.53	9.90	8.97	3.90

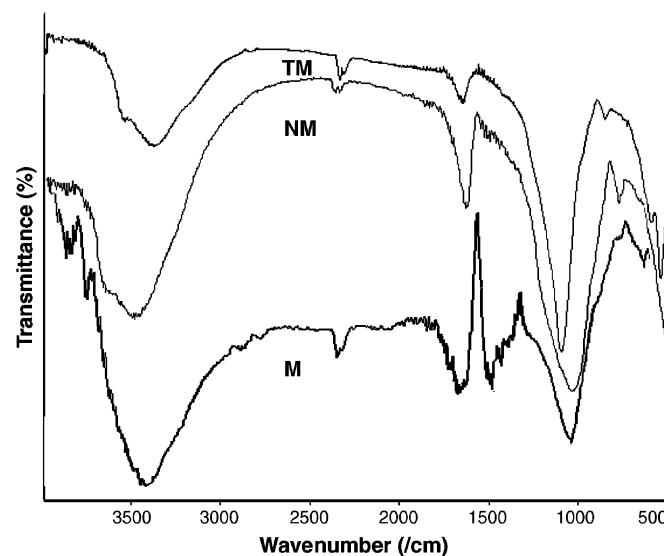


Fig. 2. FTIR pattern of parent, sodium ion exchanged and pillared montmorillonite.

non-swellaable nature. Thus, as a result of pillaring, intensity of the band around 1600 cm<sup>-1</sup> decreases [47]. The band around 1060 cm<sup>-1</sup> is due to asymmetric stretching vibrations of SiO<sub>2</sub> tetrahedra. A band around 800 cm<sup>-1</sup> is due to stretching vibration of Al<sup>IV</sup> tetrahedra, and absorption at 526–471 cm<sup>-1</sup> is due to bending of Si–O vibration. The retention of all peaks as in parent montmorillonite in the framework region clearly shows that the basic clay layer structure remains unaffected on pillaring.

### 3.4. Temperature-programmed desorption of ammonia

Acidity of the systems, tested using TPD of ammonia is shown in Table 3. Maximum acidic sites are in the weak and medium acidic regions. Pillaring causes a drastic increase in acidity; in the weak, medium and strong acidic regions. Thus, Ti pillaring enhances both Brønsted as well as Lewis sites that may cause increased activity in acid catalyzed reactions. The increase in acidity arises from the exposure of the layer structure and also due to the pillar metal oxide. Leaching of octahedral Al to interlamellar tetrahedral sites as evident from <sup>27</sup>Al NMR also results in enhanced acidity. Ion exchange also shows some increase in the total acidity. Acidity, surface area and pore volume of NM may be due to the delamination and leaching of Al<sup>3+</sup>.

Table 3  
Surface acid site distribution and total acidity obtained from TPD of NH<sub>3</sub>

Catalyst	Weak	Medium	Strong	Total 100–600 °C
	100–200 °C	200–400 °C	400–600 °C	
	(mmol/g)			(mmol/g)
M	0.0711	0.0508	0.0406	0.1625
NM	0.4795	0.1653	0.1107	0.7561
TM	0.6033	0.5057	0.2266	1.3356

### 3.5. $^{27}\text{Al}$ and $^{29}\text{Si}$ MAS NMR analysis

Plee et al. [48] have used  $^{27}\text{Al}$  and  $^{29}\text{Si}$  solid state nuclear magnetic resonance (MAS NMR) techniques to study the linkage of pillars with the clay sheets.  $^{27}\text{Al}$  NMR can detect the coordination of Al atoms in clays containing as little as 0.26% of  $\text{Al}_2\text{O}_3$  and thus is of particular utility in studying octahedral and tetrahedral sites. The resonance of montmorillonite at  $-0.83$  ppm is due to the octahedral aluminium and the one around 60 ppm is attributable to tetrahedrally coordinated Al atoms. The peak of  $\text{Al}^{\text{IV}}$  is present in sodium-exchanged and pillared system, which is due to the leaching of octahedral Al and is very weak in parent montmorillonite. During ion exchange, treatment with sodium nitrate at  $70^\circ\text{C}$  for 24 h may lead to the leaching of some  $\text{Al}^{\text{VI}}$  to interlamellar space where it exists as tetrahedral  $\text{Al}^{\text{IV}}$ . Increased intensity of  $\text{Al}^{\text{IV}}$  peak of PILC is due to the leaching of Al at

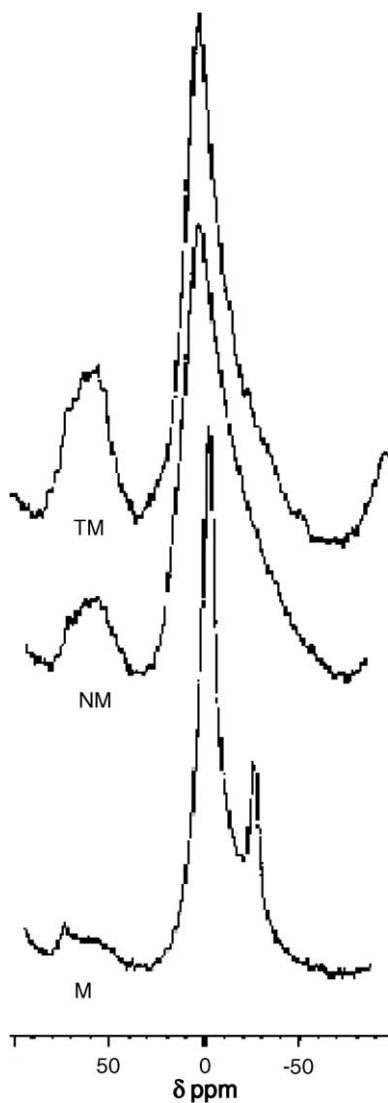


Fig. 3.  $^{27}\text{Al}$  NMR pattern of parent, sodium ion exchanged as well as pillared montmorillonite.

$70^\circ\text{C}$  and acidic conditions of the pillaring solution. For the pillared sample, small change in  $\delta$  ppm value for octahedral Al atoms may be due to the bonding of Ti atoms of intercalating polymer via oxygen atoms with the metal layers. Even though there is leaching of octahedral Al and some Al occupy in interlamellar region as tetrahedral Al (Fig. 3), the basic clay layer structure is retained.

Fig. 4 shows the  $^{29}\text{Si}$  NMR spectra of parent montmorillonite and pillared clays. In agreement with published results [49,50], the spectrum of parent montmorillonite contains two resonances. The one at  $-95.56$  ppm is attributed to T(3Si,1Al) units representing  $\text{Si}^{\text{IV}}$  atoms linked through oxygens to three other  $\text{Si}^{\text{IV}}$  and to one  $\text{Al}^{\text{VI}}$  (or Mg) in the clay octahedral layer. The second resonance near  $-110.2$  ppm is due to silica impurities present in the parent clay. On pillaring, the T(3Si,1Al) resonance shifts and broadens considerably. This upfield shift has been attributed to the diffusion of the charge compensating protons generated during calcination of the clay octahedral layer [49]. The presence of  $\text{Si}-\text{O}-\text{Ti}_{\text{pillar}}$  site may be responsible for the broadened resonance observed in the spectrum

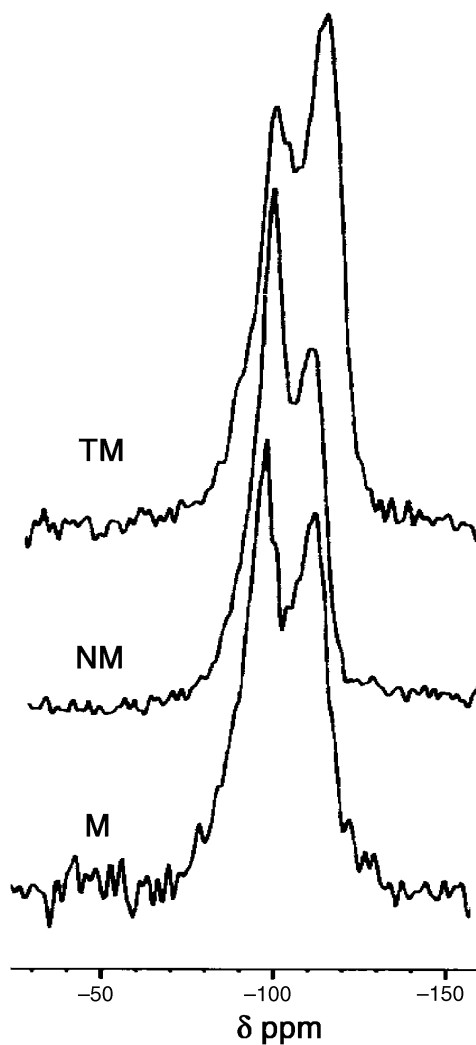


Fig. 4.  $^{29}\text{Si}$  NMR pattern of parent, sodium ion exchanged as well as pillared montmorillonite.

of PILC [51]. The  $\delta$  ppm values of different systems are shown in Table 1.

### 3.6. TG analysis

TG analysis of the oven dried (110 °C) clay samples has been performed in air atmosphere in the temperature range of 50–800 °C. Both M and NM show similar weight loss behavior in the TG analysis. TG patterns are shown in Fig. 5. The clay samples show huge weight loss in the 50–150 °C regions due to the removal of the physically adsorbed water molecules present. However at higher temperature, the weight loss is more gradual without any well-defined inflection point. These losses have been assigned to the removal of chemisorbed water, water molecules coordinated to the pillars and dehydroxylation of the pillars. The weight loss corresponding to the latter process is found to be occurring in the temperature range of 425 °C–650 °C. The dehydroxylation of the clay sheet in M and NM also occurs in this temperature range. After the complete dehydroxylation of pillars, no weight loss occurs to TM showing that the Ti-PILC is stable up to 800 °C. The clay structure collapse continues even at 800 °C in the case of M and NM. The high thermal stability of TM at 800 °C is supported by the XRD pattern shown in Fig. 1, where the peak corresponding to the expanded (100) plane is retained. The broadening and intensity reduction at high temperature is due to a minor amount of destruction occurring to the layer structure [52].

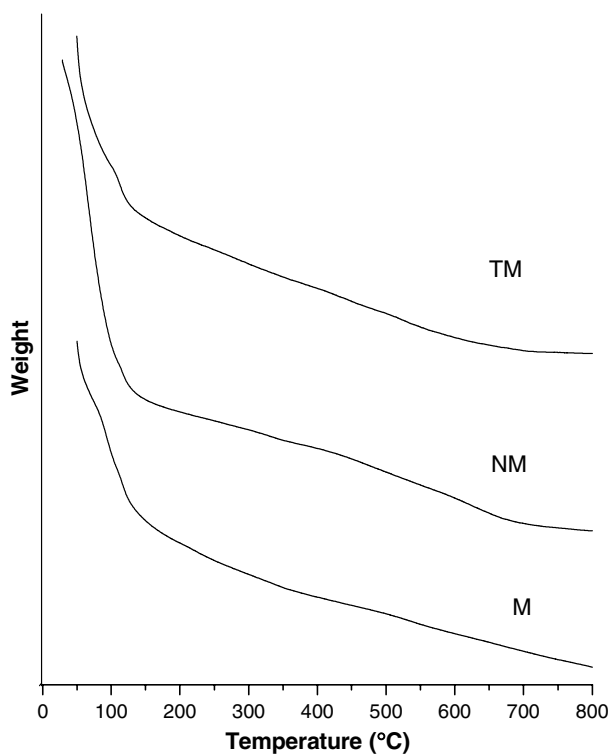


Fig. 5. TGA of parent, sodium ion exchanged and pillared montmorillonite.

### 3.7. Benzene ethylation

Ethylation of benzene is carried out over the different systems. Considering the availability, and easiness of handling, instead of ethylene we use ethanol as the alkylating agent. Here the dehydration (ethanol to ethylene) and alkylation steps are combined into one stage operation. NCL, Pune, India, developed a process called Albene technology that uses ethanol instead of ethylene in one step ethylbenzene process based on a stabilized Enclilite catalyst [53].

Vijayaraghavan and Antony Raj [54] had reported ethylation of benzene with ethanol over aluminophosphate-based molecular sieves. The various products formed include *para*- and *meta*-diethylbenzene and polyalkylated benzenes in addition to ethylbenzene. Lenarda et al. [55] reported ethylation of benzene with pillared clays. Here the alkylating agent selected is ethylene. Selectivity of ethylbenzene is found to be up to 86%. Platinum loaded zeolites reported by Kato et al. [56] showed toluene, xylene, styrene and cumene as the side products. Thus, the development of a catalyst with 100% ethylbenzene selectivity is challenging.

Optimization of reaction conditions is done over the Ti-PILC to get high conversion and selectivity in the given

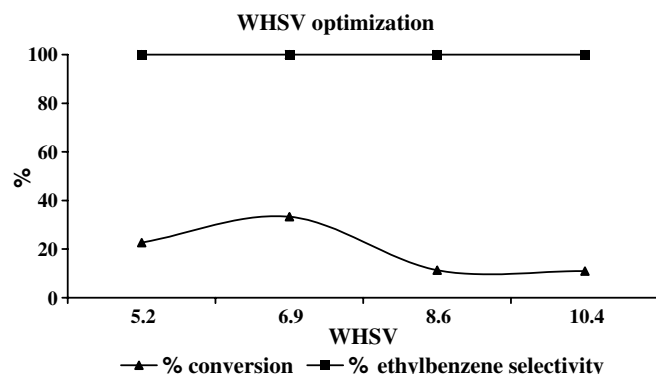


Fig. 6. Effect of WHSV at a temperature of 350 °C, benzene/ethanol molar ratio 4:1, time on stream 2 h, and catalyst weight 0.5 g.

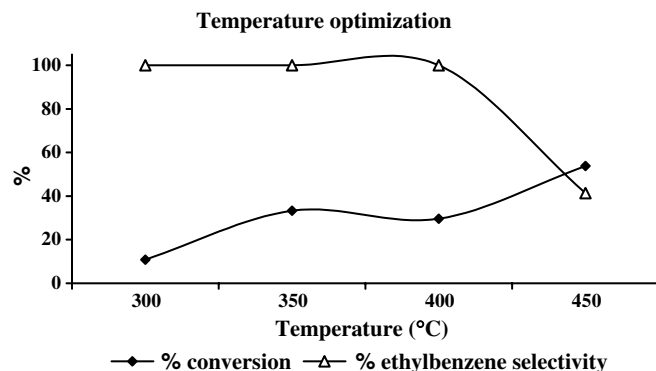


Fig. 7. Effect of temperature on conversion and selectivity at a WHSV of 6.9 h<sup>-1</sup>, benzene/ethanol molar ratio 4:1, time on stream 2 h and catalyst weight 0.5 g.

condition. Reaction is done at different WHSV at a temperature of 350 °C. It is found that in the selected conditions and WHSV, we are getting ethylbenzene as the only product and maximum conversion is obtained at a WHSV of 6.9 h<sup>-1</sup>. The results are shown in Fig. 6.

The reaction mixture is passed over the catalysts in the optimized WHSV from 300 °C to 450 °C. From Fig. 7, maximum conversion is obtained at a temperature of 450 °C with low ethylbenzene selectivity. Thus, a temperature of 350 °C is selected for further studies where ethylbenzene is the only product. The molar ratio of the feed is changed in order to get good conversion with maximum selectivity. At a molar ratio of 1:1 conversion is found to be the highest, at the expense of selectivity. *para*-Diethyl benzene is formed at this low molar ratio. At other molar ratios used, ethylbenzene is found as the only product over Ti-pillared montmorillonite and 4:1 is selected as the optimum one from the results in Fig. 8.

Performances of the present catalyst systems in the optimized conditions are shown in Table 4. Conversion is in accordance with acidity, proving the role of acidic sites for ethylation. Pillaring improves both activity as well as selectivity where M and NM gives other products such as xylene and toluene. Cracking over these catalysts leads to the side products and is found to be absent over pillared clay. The high selectivity of ethylbenzene and the absence of polyalkylbenzene over Ti-PILC in the optimized conditions may be due to the rapid diffusion of the product and the increased layer distance which allows intercalation

of more and more reactants within the layers where shape selective constraints leads to ethylbenzene as the only product. The conversion over TM is comparable with earlier reports for the ethylation of benzene with ethylene over aluminium gallium mixed pillared bentonites [55], but with increased selectivity.

Running the reaction continuously for 8 h, tests the deactivation of the catalysts. Conversion of pillared clay decreases sharply from fourth hour onwards, where both M and NM become completely inactive. 50% of the initial activity is retained and thus the coke formed is not so large as to block all the catalytically active sites of Ti-PILC. The deactivation profile is shown in Fig. 9. Regenerability of the catalysts is tested by burning off the coke formed by heating in air at 500 °C for 12 h. The initial activity is regained in pillared system whereas M and NM becomes catalytically inactive towards benzene ethylation, which may be due to the structural collapse occurring during prolonged treatment at high temperature. The regenerated PILC shows same trend towards further deactivation studies and is found to be regenerable up to four repeated cycles supporting the additional thermal stability obtained during pillaring. Fig. 10 shows the activity at a time on steam of 2 h in each regenerated cycle. The selectivity to ethylbenzene remains unaffected upon regeneration of the catalyst.

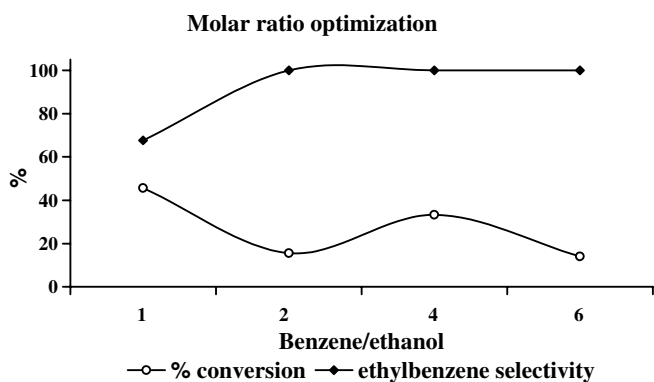


Fig. 8. Effect of molar ratio at a temperature of 350 °C, WHSV of 6.9 h<sup>-1</sup>, time on stream 2 h, and catalyst weight 0.5 g.

Table 4  
Activities of the catalysts for benzene ethylation reaction at 350 °C

Catalyst	Ethanol conversion (%)	Ethylbenzene selectivity (%)	Toluene selectivity (%)	Xylene selectivity (%)
M	12.4	43.0	25.1	32.0
NM	17.5	58.0	42.0	–
TM	30.1	100.0	–	–

Benzene/ethanol molar ratio 4:1, time on stream 2 h, WHSV 6.9 h<sup>-1</sup> and catalyst weight 0.5 g.

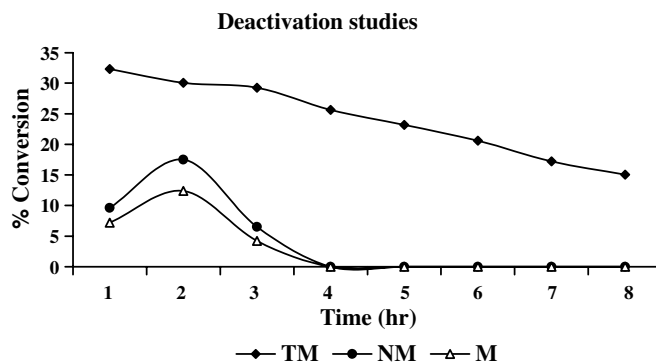


Fig. 9. Deactivation of the clay catalysts in the optimized conditions in continuous run.

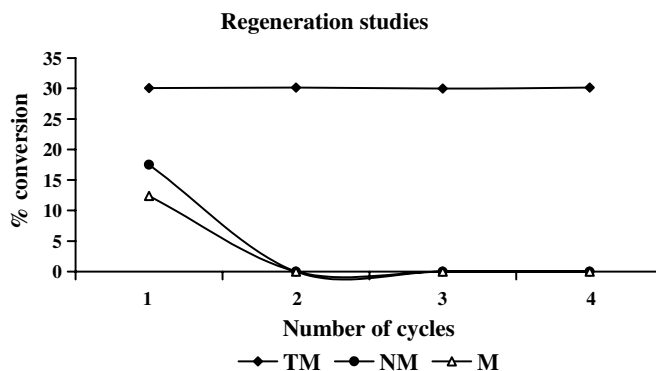


Fig. 10. Activity of different regenerated systems in repeated cycles.

#### 4. Conclusions

Ti-PILC is prepared and characterized. To the best of our knowledge, this is the first report for titania pillaring, using titania sol prepared from a precursor other than  $\text{TiCl}_4$  or titanium alkoxide. The method is found to be very effective in propping apart the clay layers as evident from XRD and surface area–pore volume analysis. Layer structure retention is proved from FTIR and  $^{27}\text{Al}$  NMR analyses. TPD of ammonia measures the acidity of catalysts. Elemental analysis data give the amount of pillar metal present. Ethylation of benzene with ethanol is carried out over the parent, ion exchanged and pillared systems. The enhanced porosity allows shape selective catalysis on Ti-PILC to form ethylbenzene as the only product.

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