

Preparation of Alumina Pillared Montmorillonite Clays Employing Ultrasonics and Their Catalytic Properties

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Abstract

An accelerated diffusion of alumina precursor species in-between the gallery region of montmorillonite clays by the use of ultrasonic technique is described. This method offers a faster, efficient and attractive route for the synthesis of alumina-pillared clay catalysts. Out of the several preparative parameters studied, the role of pre-exchanged cations influenced the optimum duration of ultrasonic agitation and treatment for the pillaring process. By comparing ultrasonic route and conventional preparation procedure, it is revealed that uniform spacing of alumina pillars in the clay means homogeneously distributed acid centers. The influence of calcination temperature on the acidity and hence the catalytic activity is described. The choice of three different montmorillonite clays with different cation exchange capacities enables one to tune the pore dimensions of the pillared clays. The catalytic applications include studies on cumene cracking, dehydration of propan-2-ol and alkylation of benzene with linear olefins.

Introduction

From the vast literature dedicated to the subject of pillared clays (PILC), a number of interesting catalytic applications, particularly for the pillared montmorillonite clays have been proposed [1,2]. However, to date, there are fewer examples wherein these versatile materials are commercially employed. The problems associated with the commercial exploitation of PILC have been addressed in various forums and out of which, the main concern is the preparation procedure of PILC [1,3]. This is because of multitudes of preparative parameters that affect the properties of the resulting PILC. The use of very diluted clay suspension makes the production route complicated and economically unattractive. Hence, there is a need for developing a rapid, cost effective and easy to scale-up and reproducible preparation procedure for PILC.

This publication highlights the synthesis of alumina pillared clays via a novel method of preparation. By studying some of the acid catalyzed test reactions, an attempt has been made to corroborate the role of the catalyst and the active sites involved. The hypothesis of the shape-selective catalysis over pillared clays is also verified.

Experimental

Three montmorillonite clay samples were used during this study as shown in Table 1. The alumina-pillaring precursor was procured from Rehies Inc. available under the trade name of chlorhydrol. The preparation of alumina-pillared montmorillonite was carried out in a following manner: A 5-wt. % aqueous suspension of clay was mixed with chlorhydrol solution so as to maintain the ratio of Al^{3+} to clay at around 20 meq. g^{-1} . This mixture was immediately subjected to ultrasonic agitation in an ultrasonic bath at ambient temperature (300 K) for 20 min. A simple ultrasonic cleaning bath (Sheshin, Japan) operating at a frequency 50 kHz was used during the pillaring process. The intercalated clay was then filtered at ambient temperature. It was then washed thoroughly with deionized water till the filtrate was free from chloride ions (AgNO_3 test). The intercalated product was dried further under vacuum and calcined at different temperatures in a programmable furnace at 10 K min^{-1} heating rate and held at the temperature for 6 h. By selecting different clay minerals and preparative conditions, a variety of pillared clay samples were prepared as listed in Table 2.

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Table 1
The clay minerals used in this study

Clay	Montmorillonite		
Source	Novasil, India	Kunipia F, Kunimine, Japan	High bond, India
Abbreviation	M1	M2	M3
Chemical composition, Mass %			
SiO ₂	69.1	64.8	61.7
Al ₂ O ₃	18.7	24.1	20.2
Fe ₂ O ₃	4.4	1.1	7.6
TiO ₂	0.4	0.1	1.0
MgO	4.2	5.8	3.5
CaO	2.9	0.3	2.2
K ₂ O	0.25	0.1	3.5
Na ₂ O	0.1	3.5	0.2
Cation exchange capacity (meq g ⁻¹)	0.75	1.15	0.35

Table 2
A summary of pillared clay samples prepared during the course of this study

No.	Parent clay	Pillared clay designation	Ultrasonic treatment time, min.	Calcination Temperature °C
1	Na-M ₁	NaPM ₁ 500	20	500
2	Ca-M ₁	CaPM ₁ 500	20	500
3	La-M ₁	LaPM ₁ 500	20	500
4	Ca-M ₁	CaPM ₁ CONV	20	500
5	Ca-M ₁	CaPM ₁ 400	(**) ¹	400
6	Ca-M ₁	CaPM ₁ 600	20	600
7	Ca-M ₂	CaPM ₂ 500	20	500
8	Ca-M ₃	CaPM ₃ 500	20	500

¹ No ultrasonic treatment, conventional method of preparation [5]

The first three pillared clay samples were prepared using M₁ clay. To study the effect of pre-exchanged cations, clay M₁ was converted into either Na or La form by repeated ion-exchange using corresponding metal nitrate solutions [4]. For comparison, one pillared clay sample (CaPM₁CONV) was prepared by conventional stirring procedure [5]. Samples CaPM₁400, CaPM₁500 and CaPM₁600 were calcined at 400, 500 and 600 °C temperatures, respectively in order to study the effect of calcination temperature on

the acidity characteristics of the pillared material, which in turn affects the catalytic properties. Finally, in order to authenticate the hypothesis of shape-selective catalysis over pillared clays, samples CaPM₁500, CaPM₂500 and CaPM₃500 were prepared using three different parent clays viz., Ca-M₁, Ca-M₂ and Ca-M₃, having different cation exchange capacities.

X-ray diffraction patterns of the powdered samples were recorded on Rigaku D Max III VC machine, using Ni-filtered Cu K α radiation. Chemical

composition of the samples was analyzed by X-ray fluorescence technique on Rigaku 3070 X-ray wavelength dispersive spectrometer. From the amount of alumina incorporation after pillaring, the number of pillars was estimated assuming that each pillar consists of 13 Al atoms.

Results and discussion

Upon converting the original Ca-M₁ clay into either Na- or La- form, the intensity of XRD peaks increased. The increased intensity could be attributed to the reorientation of the turbostratic clay layers along [001] plane. Table 3 summarizes the results of the effect of exchangeable cations on the pillared derivatives and their properties. The rate of alumina insertion is dependent on the

exchangeable cation present in the clay and hence for intercalation of optimum concentrations of alumina precursor in the clay, the extent of ultrasonic treatment (the duration) was different [7]. A 20-min ultrasonic treatment for the NaM₁ results in the delamination of the sample. This can be explained on the basis of mode of binding between these cations and the clay layers and their swelling behaviour [8]. A monovalent cation such as Na⁺, can bind with one negative charge of the layer, whereas the bivalent Ca²⁺ can bind with a charge from the opposite layer. La³⁺, a trivalent cation can impart stronger binding to the two opposite layers. In this case, the diffusion of [Al₁₃]⁷⁺ will be easier with Na-M₁ and more diffusional constraints will be experienced with Ca-M₁ or La-M₁ samples.

Table 3

Influence of pre-exchanged cations on the properties of pillared clay samples¹

Pillared clay	'd' ₀₀₁ Å	S _{BET} m ² g ⁻¹	V _μ , mLg ⁻¹	No. of pillars (x 10 ¹⁹) g ⁻¹ clay
NaPM ₁ 500 ²	-	129	0.02	8.7
CaPM ₁ 500	19.2	281	0.11	6.4
LaPM ₁ 500	17.0	155	0.06	4.0

¹ 20 minutes duration of ultrasonic agitation treatment

² No peak in XRD profile suggesting total delamination of clay

A critical comparison of the alumina pillared montmorillonite clays prepared by employing ultrasonics and a conventional synthesis method utilizing mechanical stirring (Table 4) revealed that as compared to lengthy procedures of conventional techniques, the ultrasonic preparation procedure is time effective and easy to scale-up. A higher surface area from homogeneously distributed, well-defined pores could provide better access to reactant molecules in catalytic applications. The microporous network was comparatively more stable towards thermal treatment and could even sustain in the presence of steam. Additionally, the employment of ultrasonics does not alter the inherent properties such as the acidity of the pillared clay, and hence the catalytic activity. The decomposition of propan-2-ol and cumene cracking reactions over alumina pillared clay indicate that, indeed, alumina pillared clays are acidic in nature [5-9].

When the pillared clays obtained via ultrasonic route and conventional route were compared for their deactivation in these reactions, it was found that the pillared clay catalyst prepared through ultrasonic route is more resistant to deactivation. This indicates that a uniform pillaring and hence uniform acid site distribution within the layers are achieved during ultrasonic preparation. The data given in Table 5 show that the calcination temperature affects the acidity characteristics of the pillared clays [10]. Upon increasing the calcination temperature, the Brønsted acid sites diminish rapidly as compared to Lewis acid sites. The catalyst with rich Brønsted acidity is found to be more active for cumene cracking reaction. Lewis acid sites are less active and they are more prone to deactivation. The kinetics of this reaction was studied using the first order of power law model. The kinetic parameters confirm that the catalyst calcined at lower temperature is more active for the catalytic cracking of cumene.

Table 4
Comparison of pillared clay samples prepared by ultrasonic and conventional routes

Criteria	CaPM ₁ 500	CaPM ₁ CONV
'd' ₀₀₁ Å	19.2	18.1
S _{BET} , m ² g ⁻¹	281	175
V _μ , mLg ⁻¹	0.11	0.07
No. of pillars (x 10 ¹⁹)/g clay	6.4	5.88
S _{BET} , m ² g ⁻¹ after 700 °C	237	48
Hydrothermal stability ¹ (S _{BET} , m ² g ⁻¹)	189	15
Acidity (A.U) ²	0.66	0.69
Deactivation coefficient (cumene cracking) ³	0.095	0.013
Deactivation coefficient (propan-2-ol dehydration) ⁴	0.015	0.032

¹ Hydrothermal stability test: 750 °C, 100 % steam, and 8 h.

² From chemisorption of pyridine by IR. The value is the ratio of areas of a peak of Bronsted acid sites (1550 cm⁻¹), after correction; Lewis acid sites (1450 cm⁻¹).

³ From Voorhie's law. Reaction conditions: Temperature = 300 °C, WHSV = 2.6 h⁻¹

⁴ From Voorhie's law. Reaction conditions: Temperature = 200 °C, WHSV = 3.1 h⁻¹

Table 5
Characteristics of pillared clay samples and observed reaction kinetic parameters for cumene cracking reaction

	CaPM ₁ 400	CaPM ₁ 500	CaPM ₁ 600
'd' ₀₀₁ Å	19.2	19.2	18.9
S _{BET} , m ² g ⁻¹	300	281	276
Acidity (A.U.) ¹	0.94	0.66	0.53
Conversion of cumene (wt. %)	18.4	17.9	12.0
Benzene/methylstyrene sel. ratio	1.1	0.8	0.5
Rate of reaction, (10 ³ mol s ⁻¹ kg ⁻¹)	6.5	5.0	5.3
Energy of activation, kJ mol ⁻¹	36.7	46.5	51.5
Deactivation coefficient ²	0.15	0.19	1.78

¹ From chemisorption of pyridine by IR. The value is the ratio of areas of a peak of Bronsted acid sites (1550 cm⁻¹), after correction; Lewis acid sites (1450 cm⁻¹).

² From Voorhie's law. Reaction conditions: Temperature = 300 °C, WHSV = 2.6 h⁻¹, at cumene conversion below 20 %.

In order to prepare a shape-selective pillared clay, tailor making of the pore size could be achieved by selecting parent clay with appropriate cation exchange capacity. Due to the development of uniform pore size and structure, the

pillared clays can direct a chemical transformation to yield a desired product more selectively. This is exhibited in the alkylation reaction of benzene with linear long chain olefins (Table 6).

Table 6Physical properties of the pillared clays and their catalytic activity in alkylation of benzene with linear olefins¹

	CaPM ₂ 500	CaPM ₁ 500	CaPM ₃ 500
'd' ₀₀₁ , Å	19.2	19.0	18.9
S _{BET} , m ² g ⁻¹	300	281	261
V _μ , mLg ⁻¹	0.12	0.10	0.08
Pore diameter,	6	9	11
No. of pillars (x 10 ²⁰) g ⁻¹ clay	1.21	0.64	0.35
Olefin conversion (wt. %)	100	94	83
Monoalkylation Sel. (wt.%)	72	68	50
Polyalkylation Sel. (wt.%)	28	32	50

¹ From chemisorption of pyridine by IR. The value is the ratio of areas of a peak of Bronsted acid sites (1550 cm⁻¹), Lewis acid sites (1450 cm⁻¹), after correction.

² From Voorhie's law. Reaction conditions: Temperature = 300 °C, WHSV = 2.6 h⁻¹, at cumene conversion below 20 %.

The three pillared clays with different pore characteristics yielded different amounts of mono- and poly-alkylbenzenes. The extent of polyalkylation over these catalysts was dependent on the spatial constraints in-between the layers. In the case of mono-alkylated products, although, the sizes of the possible isomers in the product are similar (2-dodecylbenzene has dimensions ca. 5.3 x 7.6 x 16.9 Å and 6-dodecylbenzene, 5.3 x 7.6 x 16.8 Å), the conformational flexibility of the isomers is different and appears to be important in determining the shape selectivity [6]. This is evident from the relative ratio of 2- to 6-dodecylbenzene obtained using pillared clay catalysts (2- / 6- dodecylbenzene ratio on CaPM₂500 was 1.4, on CaPM₁500 it was 1.3 and on CaPM₃500 catalyst, the ratio was 1.1)

The molecular graphic studies indicated that although the dimensions of alkylbenzene isomers are similar, the difference lies between the shape of the 2- and 6-dodecylbenzene isomers. Thus, through rectangular pores present in the PILC's, 2-dodecylbenzene isomer can easily diffuse out. As the chain length increases, for 2 phenyl isomers there is an increment in the 'c' direction only. The conformational changes in 2-dodecylbenzene do not alter its shape, whereas 6-dodecylbenzene does change its shape.

These conformational changes leading to the arc-like shape of the alkyl chain in 6-dodecylbenzene increase the overall strain of the molecules and hence their diffusion through pores becomes difficult [6]. Thus, this study shows that it is possible to fine-tune the 'pore' dimensions of pillared clays depending upon the need.

Conclusions

This study has opened up new dimensions in the synthesis of pillared clays by providing a novel ultrasound mediated preparation procedure. This faster route additionally offers robustness to the pillared structure, which is essential for various high temperature applications. An appropriate selection of calcination temperature provides maneuverability towards fine tuning of acidity. It is also revealed here that pillared clays can function as shape-selective catalysts. It is, indeed, possible to prepare a unique catalyst composite with desired configuration of layered materials consisting of pillars of appropriate acidity and textural characteristics.

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