

Factors affecting the preparation of alumina pillared montmorillonite employing ultrasonics

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Abstract

In the preparation of alumina pillared clays, the intercalation step is shown to be completed within a few minutes using ultrasonics, and such materials show enhanced textural properties and improved thermal stability. The role of ultrasonics and various preparative parameters that govern the preparation of alumina pillared montmorillonite are presented. This includes the effect of exchangeable cations (Na, Ca, La), three different pillaring precursors, the concentration of pillaring species, and the concentration of the clay in suspension. It is shown that the exchangeable cations and their mode of binding influence the diffusional rates of the pillaring species. When different pillaring precursors are employed, not much variation in the textural properties of pillared clays is noticed. However, their optimum concentration is essential. It is also observed that this method can handle a concentrated clay suspension for pillaring with alumina. From the kinetics of calcium exchange experiments during pillaring, it was observed that the exchange under conventional conditions is completed instantaneously, while under ultrasonic treatment only 26% of Ca^{2+} exchange took place instantaneously and further exchange occurred only after ultrasonic treatment. From these observations, it is proposed that the role of ultrasonics in the present synthesis is the acceleration of diffusion of the intercalating aluminium pillaring species followed by an ion exchange process. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

‘Pillaring of clays’ is a process by which it is possible to convert inexpensive and thermally unstable clay minerals into highly porous and stable structures. In this process, robust oxide particles are formed between the clay layers, which act as pillars, preventing the collapse of the expanded layers. Although the initial impetus for the development of pillared clays (PILCs) was

their use as cracking catalysts [1], alumina and other oxide pillared clays have now been found to be active in a number of other catalytic reactions [2]. The possibility of generating diversified properties by making use of various clay minerals, pillar oxides and pre-/post-treatments has opened up new dimensions of research. This includes the field of catalysis and also other emerging fields, like separation sciences, sorption, sensors, thermal insulation, electrodes and various environmental issues [3]. The recent announcement of a large-scale production of pillared clays to be used as catalytic materials and as sorbents by the British

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Technology Group [4] has renewed further interest in these versatile materials. Eventually, what really hinders the commercial exploitation of these materials are the complicated and lengthy preparation procedures and thermal instabilities. In spite of exhaustive studies on the synthesis methods for PILCs, very few of them have promising utility from the industrial viewpoint [5–7].

Recently, we have reported a novel preparation method for PILCs wherein the time-consuming intercalation step can be completed within a few minutes at ambient temperature by employing ultrasonics [8]. It was also shown that the structural, textural and catalytic properties of PILCs derived from the ultrasonic route are superior to those prepared by conventional pillaring procedures [9]. We have attempted to understand the effect of various preparation parameters that influence the preparation of PILCs, and also the role of ultrasonics, which accelerates the synthesis. Various preparative parameters have been evaluated. The results are presented in this communication.

2. Experimental

For this study, a commercial montmorillonite clay with chemical composition SiO_2 69.1, Al_2O_3 18.7, Fe_2O_3 4.4, TiO_2 0.37, MgO 4.19, CaO 2.93, K_2O 0.25, Na_2O 0.07 (mass%) was used. The cation exchange capacity (CEC) was found to be 0.75 meq g^{-1} . The specific surface area of $78 \text{ m}^2 \text{ g}^{-1}$ arose from a broad range of pore sizes. An ultrasonic bath (Sheshin, Japan, 50 kHz) was used, in which a mixture of an aqueous clay suspension and the pillaring species was treated for different intervals of time. The intercalated material was separated by filtration and dried under vacuum at room temperature. It was then heated to 773 K in a programmable furnace at 10 K min^{-1} and further calcined for 6 h at this temperature.

The X-ray diffraction (XRD) profiles were obtained on a Rigaku D Max III VC instrument using Ni-filtered $\text{Cu K}\alpha$ radiation. The samples were powdered and pressed. The chemical composition of the samples was determined by X-ray

fluorescence on a Rigaku 3070 X-ray wavelength dispersive spectrometer. From the amount of alumina incorporated, the number of pillars per gram of raw clay was calculated assuming that every incorporated Al forms a pillar and each of the pillars is made up of 13 Al atoms. To determine the precise concentration of exchangeable cations, an atomic absorption spectrometer (Hitachi Z8000, Polarized Zeeman Spectrophotometer) was used. Nitrogen adsorption experiments were carried out at 77 K using a continuous volumetric instrument (Omnisorp 100 CX, Coulter). Prior to the adsorption experiments, all samples were degassed at 523 K for 6 h. The surface area (S_{BET}) was calculated in the relative pressure range (p/p_0) of 0.001 to 0.1. The micropore volume (V_{μ}) was estimated from the t -plot.

To study the influence of exchangeable cations on the textural properties of the PILCs and the optimum duration of the ultrasonic treatment, a part of Ca-clay (Ca-M) was converted into the Na and La forms (Na-M and La-M) by repeated ion exchange using the corresponding metal nitrates solutions. The PILCs derived from each form of clay are designated, for example, Na-PC-5. The number 5 denotes the duration in minutes of the ultrasonic treatment. The optimum samples obtained from each form were further evaluated for their thermal stability (the samples were heated at 773, 973 and 1173 K for 8 h) and hydrothermal stability (1023 K, 100% steam, 8 h).

Three pillaring precursors were used in this study. These are NaOH hydrolyzed $\text{Al}(\text{NO}_3)_3$ (OH/Al^{3+} mole ratio = 2), an aqueous solution of ACH[®] (Reheis Chemical Co., USA) and that of Takibin[®] (Taki Chemicals Co., Japan). The interest was to study whether ultrasonically accelerated intercalation is dependent on various Al species that are present in the above solution. The effect of the concentration of ACH was studied by varying the Al^{3+} to clay ratio in steps of 10, 20, 30 and 40 meq g^{-1} clay. To study the effect of the clay concentration, 5, 10 and 20 wt% of aqueous suspensions of Ca-M were used for pillaring.

The kinetics of calcium exchange during pillaring were performed in situ in the following manner: a 5% aqueous suspension of Ca-M was mixed with an aqueous solution of ACH in the ratio of

20 meq g⁻¹. The mixture was immediately subjected to ultrasonic or conventional stirring treatment for 20 min. After every 5 min, a small aliquot (0.5 cm³) was withdrawn and analysed for its Ca concentration by AAS. After 20 min, the intercalated material was filtered and washed thoroughly. The filtrate and washings collected together were analysed for their Ca content.

3. Results and discussion

3.1. Effect of exchangeable cations and duration of the ultrasonic treatment on the textural properties of the PILCs

Upon converting the original Ca-M clay either into its Na or La form, the intensity of the XRD peaks increased. The increased intensity could be attributed to the reorientation of the turbostatic clay layers along the [001] plane. It was observed that, after pillaring and calcination, the intensity of the [001] peak was reduced by almost 10%, with a similar level of increment in the full-width at half-maxima (FWHM) of the reflection. This suggests some loss of lamellaricity (layer stacking order) and an enlargement in the overall particle size. Table 1 summarizes the results of the effect of exchangeable cations on the pillared derivatives and the optimum duration of the ultrasonic treat-

ment required. If the duration of the ultrasonic treatment was increased, more alumina was incorporated into all clays. The rate of alumina insertion is dependent on the exchangeable cation present in the clay. For similar durations of ultrasonic treatment (ca. 5 min), the alumina incorporation seems to increase in the order Na-M > Ca-M > La-M. This can be explained on the basis of the mode of binding between these cations and the clay layers and their swelling behaviour [10]. A monovalent cation like Na⁺ can bind with one negative charge of the layer, whereas the bivalent Ca²⁺ can bind a charge from the opposite layer as well. 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-M, and more diffusional constraints will be experienced with Ca-M or La-M. However, it must be noted that, in the case of La-M, total exchange of La was not achieved. Around 8% of the initial amount of La was found in the PILC. Tokarz and Shabtai [11] reported around 30% retention of La when the La form of montmorillonite was pillared with alumina. In a way, the present method is found to be more effective compared with the conventional techniques of pillaring.

The surface area and micropore volume initially increase and then again decrease during the ultrasonic treatment. Of course, these maxima are dependent on the form of the clay and the duration

Table 1
Effect of exchangeable cations and duration of ultrasonic treatment required for optimum PILC materials^a

US time ^b (min)	Na-M ^c				Ca-M				La-M			
	<i>d</i> ₀₀₁ (Å)	No. of pillars ^d	S _{BET} (m ² g ⁻¹)	V _μ (cm ³ g ⁻¹)	<i>d</i> ₀₀₁ (Å)	No. of pillars ^d	S _{BET} (m ² g ⁻¹)	V _μ (cm ³ g ⁻¹)	<i>d</i> ₀₀₁ (Å)	No. of pillars ^d	S _{BET} (m ² g ⁻¹)	V _μ (cm ³ g ⁻¹)
2	18.3	5.2	108	0.03	14.1	3.2	82	–	14.0	2.8	80	–
5	18.6	7.0	236	0.09	16.0	4.4	100	0.02	14.2	3.1	86	–
10	18.4	8.1	180	0.05	18.3	5.6	119	0.04	16.0	3.6	135	0.03
20	–	8.7	129	0.02	19.2	6.4	281	0.11	17.0	4.0	155	0.06
40	–	8.8	132	0.02	18.3	7.4	212	0.08	17.7	4.5	200	0.06
60	–	8.9	130	–	17.6	8.9	165	0.06	18.6	5.1	255	0.08
80	–	9.0	128	–	–	9.1	200	0.03	19.0	5.7	260	0.10

^a 5% clay suspension, 20 meq g⁻¹ of ACH.

^b Ultrasonic treatment duration.

^c Montmorillonite clay.

^d No. of pillars (× 10¹⁹) g⁻¹ clay.

of the ultrasonic treatment. As can be seen, for a monovalent form of clay (Na-M) the optimum duration of the ultrasonic treatment is shorter. The duration needed for an effective pillaring increases with the valency of the exchangeable cation. Upon increasing the duration of the ultrasonic treatment, the hydrated exchangeable cations, in the presence of very strong diffusional forces, can no longer hold the layers together, leading to layer dispersion. Such a clay, upon drying and calcination, exhibited no (001) reflections and less microporosity. The resulting material is said to be a 'delaminated clay' instead of a 'pillared clay' [12]. The delamination occurs at different durations of ultrasonic treatment for a given form of clay. For Na-M, the delaminated product was formed after 20 min of ultrasonic treatment. A longer ultrasonic treatment is required (>60 min) to delaminate Ca-M. No delamination was observed in the case of La-M up to 80 min.

The pillared materials prepared at optimum conditions of ultrasonic treatment from the three different forms of the clay, viz. Na-PC-5, Ca-PC-20 and La-PC-80, were subjected to thermal and hydrothermal stability tests. The results are presented in Table 2. Indeed, there was a considerable reduction in the surface area for all the PILC samples above 973 K. Similarly, when subjected to steaming treatment, these materials could retain their surface area in the range of 42 to 65% of the initial value. For Na-PC-5 at 973 K, a surface area reduction of 33% was observed. At similar conditions a drop of 15% for Ca-PC-20 and 23% for

La-PC-80 was observed. Among the three pillared samples, Ca-PC-20 possesses the maximum thermal stability. The stability of the pillared material depends upon effective pillaring and the uniform distribution of the pillars within the clay layers. In the case of a clay of 0.75 meq g^{-1} CEC, theoretically 6.4×10^{19} pillars g^{-1} clay can be formed. It is known that ACH solution contains $[\text{Al}_{13}]^{7+}$ along with monomeric Al species [12]. In the case of Na-PC-5, the small monomeric species will diffuse rapidly, within 5 min of ultrasonic treatment, thereby blocking the exchange sites. In such cases, there would be fewer effective pillars, leading to poor stability of the pillared material. On the other hand, incomplete exchange of La will produce non-uniformity in pillar spreading, and at elevated temperatures the material La-PC-80 is destabilized. Thus, it is seen that the exchangeable cations strongly govern the textural properties of the pillared clays and that the effect must be considered while optimizing the preparation parameters.

3.2. Effect of the pillaring precursors, their concentration and the clay concentration

When different Al pillaring precursors were used for pillaring of Ca-M under ultrasonic treatment of 20 min, no big differences were observed in the textural properties of the pillared derivatives. In spite of the large variations in the constitution of the pillaring precursors, the surface area and microporosity of the PILCs were not affected (Table 3).

Table 2
Thermal and hydrothermal stability tests on PILCs derived from different exchangeable cationic forms of montmorillonite

Temperature (K) ^a	Na-PC-5 ^b			Ca-PC-20			La-PC-80		
	d_{001} (Å)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{μ} ($\text{cm}^3 \text{g}^{-1}$)	d_{001} (Å)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{μ} ($\text{cm}^3 \text{g}^{-1}$)	d_{001} (Å)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{μ} ($\text{cm}^3 \text{g}^{-1}$)
773	18.6	236	0.09	19.2	281	0.11	19.0	260	0.1
973	17.8	157	0.07	18.3	237	0.09	17.6	200	0.08
1173	17.5	48	0.01	17.6	61	0.02	17.0	53	0.02
1023, 100% steam	18.0	100	0.02	18.1	181	0.06	18.1	157	0.04

^a Thermal treatment for 8 h.

^b Number denotes the duration in minutes of ultrasonic treatment.

Table 3

Use of different pillaring species and their effect on the textural properties of the PILC^a

Pillaring species	' d_{001} ' (Å)	No. of pillars ^b	S_{BET} (m ² g ⁻¹)	V_{μ} (cm ³ g ⁻¹)
AlCl ₃ + NaOH	19.0	6.2×10^{19}	260	0.10
'ACH'	19.2	6.4×10^{19}	281	0.11
'Takibine'	19.1	6.2×10^{19}	278	0.10

^a Ca-M clay, Al³⁺/clay ratio = 20 meq, ultrasonic treatment of 20 min.^b No. of pillars ($\times 10^{19}$) g⁻¹ clay.

The chemistry of the effective pillaring species, [Al₁₃]⁷⁺, is well documented [13]. It is also known that different pillaring precursors consist of different concentrations of Al hydroxy species [14]. Pinnavaia et al. [12] have shown that, although base-hydrolyzed Al and commercial ACH contain different species, the pillared derivatives possess similar textural and catalytic properties. As reported earlier [12], the pillaring precursors do not alter the PILCs with respect to their textural and catalytic properties. Similar observations were made in the present study using ultrasonics. The pillaring precursors selected for this purpose, i.e. base-hydrolyzed Al(NO₃)₃, ACH and Takibine, showed the presence of different Al species as observed in ²⁷Al liquid NMR studies. The corresponding PILCs showed no significant variation in the textural properties of the samples as depicted in Table 3. It can be concluded, therefore, that ultrasonically assisted pillaring has no selectivity with respect to the nature of species that are present in the solution.

Another factor which affected the preparation was the concentration of the pillaring species as shown in Table 4. When a dilute ACH solution was used as pillaring precursor, the PILC products ended up with poor textural properties in terms of

surface area and microporosity, in spite of the successful intercalation as evident from the basal spacing. It is well documented that when dilute pillaring species are used, the effective [Al₁₃]⁷⁺ moiety undergoes excessive hydrolysis, giving rise to smaller species [15,16]. In such cases, the maximum alumina incorporation would be observed. In other words, smaller Al species diffuse rapidly, thereby forming irregular pillar distribution. Upon using a very concentrated pillaring solution, further polymerization of [Al₁₃]⁷⁺ takes place due to molecular association. The intercalation of such species becomes more difficult, and hence less alumina incorporation was recorded. As recommended by Harris [15], an aging period of 10 days is essential to obtain a pillared clay with optimum properties. In the present work, no aging time was allowed, and thus the role of aging of the pillaring species remains unascertained. The necessity of aging of the pillaring species was also questioned by Pinnavaia et al. [12].

In Table 5, the results obtained from using suspensions of different clay concentration studies are presented. The use of concentrated clay suspension has also been found to be effective under this preparation method. A sharp peak corresponding to ' d_{001} ' around 19 Å in the X-ray diffraction

Table 4

The effect of concentration of 'ACH' on the textural properties of the PILC^a

Al ³⁺ (meq g ⁻¹ clay)	' d_{001} ' (Å)	No. of pillars ^b	S_{BET} (m ² g ⁻¹)	V_{μ} (cm ³ g ⁻¹)
10	18.9	6.9×10^{19}	170	0.06
20	19.2	6.4×10^{19}	281	0.11
30	18.7	5.2×10^{19}	233	0.08
40	18.7	4.0×10^{19}	226	0.08

^a Ca-M clay, Al³⁺/clay ratio = 20 meq, ultrasonic treatment of 20 min.^b No. of pillars ($\times 10^{19}$) g⁻¹ clay.

Table 5
The effect of clay concentration on the textural properties of the PILC^a

Clay concentration (wt%)	d_{001} (Å)	No. of pillars ^b	S_{BET} (m ² g ⁻¹)	V_{μ} (cm ³ g ⁻¹)
5	19.2	6.4×10^{19}	281	0.11
10	19.1	5.8×10^{19}	275	0.10
20	19.1	5.0×10^{19}	232	0.09

^a Ca-M clay, Al³⁺/clay ratio = 20 meq, ultrasonic treatment of 20 min.

^b No. of pillars ($\times 10^{19}$) g⁻¹ clay.

profiles indicated the success of pillaring when the clay (Ca-M) concentration was increased from 5 to 20 wt%. When the clay concentration was increased, the number of pillars introduced was found to decrease. A marginal reduction in the surface area was also observed. This may be due to the fact that in concentrated clay suspensions the clay particles tend to agglomerate, thereby reducing the internal surface available for the intercalation. In these experiments, pillaring was carried out over 20 min of ultrasonic agitation. It will be interesting to study whether one can get the optimum results either by increasing the duration of the ultrasonic treatment or the intensity of the ultrasonic source. Such work is underway and at this stage it may be noted that the present method can handle a concentrated clay suspension, which is interesting for the large-scale production of alumina PILCs.

3.3. The role of ultrasound in the present preparation

The pillaring or intercalation step in the case of smectite clay-like materials is known to be driven by two processes: i.e. the diffusion of the pillaring species and the ion exchange phenomenon. Plee et al. [17] reported that the saturation of negative charges by small Al species is the first reaction, followed by the diffusion of [Al₁₃]⁷⁺ species. During the preparation of delaminated clays in the presence of polyvinyl alcohol, Suzuki et al. [18] observed that ion exchange precedes the introduction of the pillaring precursors. Figueras et al. [19] found that the fast ion exchange process is limited by the diffusion of Al₁₃. Thus, it was interesting to know whether ultrasound assists faster diffusion or favors rapid ion exchange. A

comparison of the exchange process during alumina pillaring of Ca-M by using ultrasound (curve a) and a conventional method of stirring (curve b) is shown in Fig. 1. The kinetics of calcium exchange during pillaring (Fig. 1) show that the concentration of exchangeable cations coming out during the ultrasonic treatment is lower (curve a). When Ca-M is pillared, around 26% of the Ca is exchanged during the first 5 min of ultrasonic treatment. This degree of exchange during the first few minutes of ultrasonic treatment is probably restricted to the Ca ions that are present on the outer layers of the clay particles. There was no substantial change in the Ca concentration from 5 min to 20 min of ultrasonic treatment. All the Ca present in the parent clay came out in the solution only at the end of ultrasonic treatment and during filtration and washing. On the other hand, when the mixture of pillaring species and clay suspension is stirred for 20 min following a conventional procedure, the ion exchange of Ca takes place first (curve b). The complete Ca

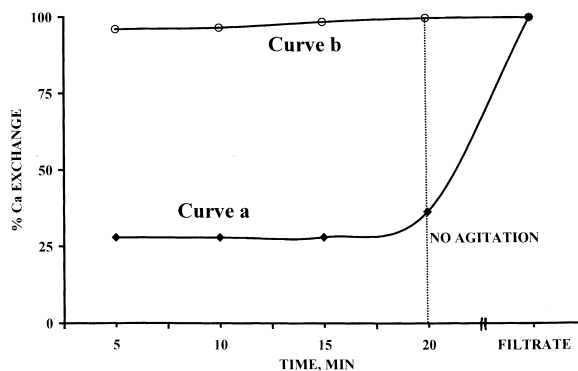


Fig. 1. Comparison of calcium exchange during pillaring of Ca-montmorillonite by ACH solution using ultrasonic treatment (curve a) and a conventional method of stirring (curve b).

exchange occurs within a very short period of time. The accelerated intercalation employing ultrasound has also been reported [20–22]. Sivakumar et al., [20] used this technique to intercalate boehmite sol into Na-montmorillonite. The report by Kooli et al. [21] deals with the preparation of the decavanadate-exchanged pillared layered double hydroxide (LDH) under an ultrasonic treatment of 120 min. Hu et al. [22] reported the intercalation of heteropolyoxometalate anionic species into LDH within 7 min of ultrasonic agitation. A plausible explanation for the accelerated intercalation could be the *microstreaming effect* known in sonochemistry. It is known that, when a solid–liquid mixture is treated ultrasonically, the cavitation bubbles formed in the rarefaction cycle undergo unsymmetric collapse near the solid surface, which causes ‘in-rush’ of the liquid into the solid. This effect is called ‘microjet formation’ or ‘microstreaming’, wherein the velocity of the in-rushing liquid is as high as 100 m/s. This is the reason why ultrasound is more effective for cleaning [23,24].

In the present synthesis, the in-rushing liquid contains pillaring species and, obviously, their diffusion inside the clay layers is accelerated. Further, according to our presumption, if the in-rush of liquid is so powerful, Ca ions may not come out till the ultrasonic treatment is in progress. Hence, the ion exchange step can take place in the absence of ultrasonic treatment. Two inferences can be drawn from this study. First, the use of ultrasound assists only diffusion of the pillaring species and not the ion exchange. In the first instance, the bulky pillaring species are stuffed inside the clay. Second, the ion exchange process is completed subsequent to the intercalation step during post-ultrasonic treatment of aging of the suspension.

4. Conclusions

A rapid and efficient preparation of PILCs could be achieved using ultrasonic agitation treatment. The study has shown that the optimum duration of the ultrasonic treatment required for pillaring is influenced by the exchangeable cations,

which in turn affect the textural properties of the resulting PILCs. These cations (Na^+ , Ca^{2+} and La^{3+}) are known to have a specific association with the clay layers. The pillaring species can diffuse easily when the clay is in the monovalent form. The diffusion is retarded when the polyvalent cations are present in the clay. However, the optimum samples derived from either the mono-, di- or trivalent cation form of the clay behave differently when subjected to stability tests. The present preparation method can also handle concentrated clay suspensions, which is advantageous over the conventional preparation methods, where the use of dilute suspension causes handling problems. The nature of the pillaring species seems not to be an important factor for the preparation of PILCs. Although they differ greatly with respect to their compositions, it can be said that during intercalation there are a lot of changes with respect to the charge of the pillaring species, their structure, etc. From the kinetics of calcium exchange during pillaring, it appears that the intercalation step is strongly accelerated when ultrasonic treatment is employed. The role of ultrasound is to accelerate the $[\text{Al}_{13}]^{7+}$ diffusion within the clay layers.

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References

- [1] D.E.W. Vaughan, R.J. Lussier, J.S. Magee, US Patent 4176090, 1979.
- [2] R. Szostak, C. Ingram, *Stud. Surf. Sci. Catal.* 94 (1995) 13.
- [3] I.V. Mitchell (Ed.), *Pillared Layered Structures*, Elsevier Applied Science, New York, 1990.
- [4] *Industrial Minerals* (1995) 77.
- [5] A. Sanchez, M. Montes, *Micropor. Mesopor. Mater.* 21 (1998) 117.
- [6] G. Poncelet, R. Molina, A. Vieira-Coelho, *Clays Clay Miner.* 40 (1992) 480.
- [7] L. Storaro, M. Lenarda, R. Ganzerla, A. Rinaldi, *Micropor. Mater.* 6 (1996) 55.
- [8] S.P. Katdare, V. Ramaswamy, A.V. Ramaswamy, *J. Mater. Chem.* 7 (1997) 2197.

- [9] S.P. Katdare, V. Ramaswamy, A.V. Ramaswamy, *Catal. Today* 49 (1999) 313.
- [10] K. Norrish, *Discuss. Faraday Soc.* 18 (1954) 120.
- [11] M. Tokarz, J. Shabtai, *Clays Clay Miner.* 33 (1985) 89.
- [12] T.J. Pinnavaia, M.S. Tzou, S.D. Landau, R.H. Raythatha, *J. Mol. Catal.* 27 (1984) 195.
- [13] R. Burch, *Catal. Today* 2 (1988) 185.
- [14] J.W. Akitt, A.A. Farthing, *J. Chem. Soc., Dalton Trans.* (1981) 1624.
- [15] J.R. Harris, in: L. Occelli (Ed.), *Fluid Catalytic Cracking: The Role in Modern Refinery*, ACS Symp. Ser. No. 375, American Chemical Society, Washington, DC, 1988, p. 253.
- [16] R.A. Schoonheydt, J. van den Eynde, H. Tubbax, H. Leeman, M. Stuyckens, I. Lenotte, W.E.E. Stone, *Clays Clay Miner.* 41 (1993) 598.
- [17] D. Plee, L. Gataineau, J.J. Fripiat, *Clays Clay Miner.* 35 (1987) 81.
- [18] K. Suzuki, T. Mori, K. Kawase, H. Sakami, S. Iida, *Clays Clay Miner.* 36 (1988) 147.
- [19] F. Figueras, Z. Klapys, P. Massiani, Z. Mountassir, D. Tichit, F. Fajula, *Clays Clay Miner.* 38 (1990) 257.
- [20] S. Sivakumar, A.D. Damodaran, K.G.K. Warriar, *Ceram. Int.* 21 (1995) 85.
- [21] F. Kooli, W. Jones, V. Rives, M.A. Ulibarri, *J. Mater. Sci. Lett.* 16 (1997) 27.
- [22] C. Hu, X. Zhang, Q. He, E. Wang, S. Wang, Q. Guo, *Trans. Met. Chem.* 22 (1997) 197.
- [23] T.J. Mason, *Chem. Soc. Rev.* 26 (1997) 443.
- [24] L.H. Thompson, L.K. Doraiswamy, *Ind. Eng. Chem. Res.* 38 (1999) 1215.