Catalysis Letters 43 (1997) 133–137

Preparation and characterization of sulfated titanium-modified pillared montmorillonite

H.L. del Castillo, A. Gil[a] and P. Grange

Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix de Sud, 2/17,
1348 Louvain-la-Neuve, Belgium
[a] *Departamento de Química Aplicada, Universidad Pública de Navarra, Campus de Arrosadía, 31006 Pamplona, Spain*

Received 5 June 1996; accepted 2 October 1996

Sulfated titanium-modified pillared montmorillonites using $(NH_4)_2SO_4$ and H_2SO_4 have been prepared. The influence of the method of sulfation and of the SO_4^{2-}/Ti mole ratio was studied. An important effect in both the basal spacings and the acidic properties was observed when $(NH_4)_2SO_4$ or H_2SO_4 is present in the solution of intercalation. When titanium pillared clays (Ti-PILCs) are sulfated by impregnation, their acidity initially increases, irrespective of the sulfate source, whereas their basal spacings are not modified. A loss of specific surface area is observed when the temperature of calcination or the SO_4^{2-}/Ti mole ratio is increased.

Keywords: sulfated titanium-modified pillared montmorillonite, acidity modification, acidity characterization

1. Introduction

In the last years, several types of solids with strong acidity have been developed and applied to catalytic reactions. The routes conducting these solids have followed several approaches. In particular, the promotion of oxides, such as ZrO_2, TiO_2 and Fe_2O_3, with sulfate gives strong acidic solids. When pillared clays are considered, the first reports on sulfation have been made by Farfan et al. [1], Khalfallah Boudali et al. [2], Clearfield et al. [3] and Bouchet et al. [4].

Since the first works of intercalation of inorganic molecules in smectite by Barrer and McLeod [5] and inorganic molecules by Vaughan [6], a broad variety of inorganic hydroxycations have been successfully intercalated in smectites. The inorganic hydroxycations are obtained by hydrolysis of metal oxides or salts, which upon dehydration and dehydroxylation thermal conditions give stable metal oxide clusters which act as pillars keeping the silicate layers separated. Organometallic compounds, which upon hydrolysis and calcination give metallic oxides, are also used in the intercalation of clays. These pillared intercalated clays (PILCs) combine acidity, regular porosity and relatively high thermal stability, making them similar to zeolite-like materials. The main early interest in PILC was in the possibility of replacing zeolites as catalyst for fluidized catalytic cracking [7]. However, this possibility has been hindered and other potential uses for these materials, such as catalysts, catalyst supports, molecular sieves and adsorbents, have been considered.

Polymeric compounds of Al, Cr and Zr are among the principal pillaring species quoted in the literature. In spite of the interesting catalytic properties of TiO_2, Ti-PILCs have received considerably less attention than other oxide pillared clays. Consequently, only a few preparation methods for titanium pillared clays have been reported [2,8–13]. These studies indicate that the preparation conditions are critical due to the diversity of titanium species formed in aqueous solutions.

Acidity (Brønsted or Lewis) is an important property of the PILCs. It was shown that on heating above 773 K the Brønsted acid sites are destroyed and the resulting pillared clays have mainly Lewis acid sites [14–16]. Thus, there is a need to increase the Brønsted acidity for reactions to be carried out at temperatures lower than those required for catalytic cracking. A general procedure is the addition of sulfate or phosphate ions to the pillared clays [1–4,17]. A variety of techniques have thus been reported in the literature with the aim of introducing SO_4^{2-} ions on the surfaces of metal oxides. Among them are impregnation with a $(NH_4)_2SO_4$ or H_2SO_4 solution, as well as treatment with SO_3, SO_2 or H_2S followed by oxidation [18]. These treatments modify the properties of the PILCs and it is necessary to check if these treatments affect the clays sheet and/or the pillars. In this way, it is known that the acid activation of clays affects the structure of the clay by leaching out Al^{3+}, Mg^{2+}, Fe^{3+} and other cations that are present in both octahedral and tetrahedral layers, and also the lattice silicon, which can be converted to a more amorphous phase [19–21]. The nature of the resulting acid-treated clays is determined by the properties of the original clay (the degree of isomorphous substitution, the nature of exchangeable cations present, the nature and the amounts of impurities which are present) [21–23] as well as the activation conditions (type and amount of acid, temperature, time of activation) [23–26]. These treatments also affect the pillars of PILCs by leaching out cations as a function of the chemical nature of the pillars.

The nature and properties of the acid sites of PILCs are still not well known [15,16,27,28]. The acidity and acid site types (Lewis and Brønsted) depend on the exchanged cations [27], the preparation method [16,27,29,30], and the nature of the starting clay [31]. It is well known that Lewis acidity in alumina pillared montmorillonites is due to two types of sites, both ascribable to aluminium centers [32] which are related to aluminium sites in the tetrahedral layer of the clay and with aluminium sites on pillars. This last one is currently related to the Lewis type [16,30,33,34]. On the other hand, the origin of Brønsted acid sites in pillared clays is still not clear. Several sources for Brønsted acidity have been discussed in the literature: (i) the structural hydroxyl groups in the clay layer from the initial sites of ion exchange [16,31,35,36]. The most likely proton site for some smectites is located at the Al(VI)–O–Mg linkage [35]. For other clays, the proton sites are located at the Si–O–AlOH groups resulting from isomorphous substitution of Si by Al in the tetrahedral layer [31,36]; (ii) the protons derived from the cationic oligomers which, upon heating, decompose into metal oxide pillars and liberate protons [2,27,29]; (iii) a synergy phenomenon between the siliceous clay sheet and the pillar [15,32,37].

In the present work, the preparation and characterization of two series of sulfated titanium-modified pillared montmorillonites have been studied. The sulfation of the pillared clays has been carried out by impregnation of a Ti-PILC and by intercalation in presence of $(NH_4)_2SO_4$ or H_2SO_4 in the solution. In order to characterize the samples, the evolution with the SO_4^{2-}/Ti mole ratio of the basal spacings, specific surface areas and total acidity (amount of NH_3 desorbed) have been considered.

2. Experimental

The starting material used was montmorillonite (Kunipia F), kindly supplied by Kunimine Co. This montmorillonite was dispersed in water and aged for at least two months. The suspension was then washed by dialysis and the solid content of the dialyzed clay dispersion was 10 g ℓ^{-1}.

The preparation of the intercalating solution of titanium involved the slow addition of titanium tetraethoxide to a 5 M HCl solution under vigorous stirring, so that the H/Ti mole ratio was equal to 2 [8]. This solution was used for intercalation without prior ageing. The titanium solution was added to the aqueous montmorillonite suspension (pH = 1.4) at a ratio of 10 mmol Ti (g of clay)$^{-1}$. The solid was kept in contact with the solution at room temperature for 3 h, washed by centrifugation, dried at 393 K and then calcined at 673 K.

In order to prepare the sulfated titanium-modified pillared clays, the above titanium pillared montmorillonite before the calcination at 673 K was treated with a 0.1 N $(NH_4)_2SO_4$ (SN(Ti-PILC)) or a 0.1 N H_2SO_4 (SH(Ti-PILC)) solution. In both cases, the SO_4^{2-}/Ti molar ratios were 0.025, 0.075, 0.25 and 0.75. These solids were washed by centrifugation, dried at 393 K and calcined at 673 K for 8 h. A similar procedure was used to prepare sulfated titanium-modified pillared clays. 0.1 N $(NH_4)_2SO_4$ (SNTi-PILC) or 0.1 N H_2SO_4 (SHTi-PILC) solutions were added to the titanium solution used for intercalation. In both solutions, the SO_4^{2-}/Ti molar ratios were also 0.025, 0.075, 0.25 and 0.75. After 3 h of reaction, the solids were washed by centrifugation, dried and calcined as previously reported.

The basal spacing of the samples was measured by X-ray diffraction (XRD) on a thin layer of the clay deposited on glass slides using a Kristalloflex 805 – Siemens diffractometer with Ni filtered Cu K_α ($\lambda = 1.5418$ Å) radiation.

Nitrogen adsorption experiments were performed at 77 K using a static volumetric apparatus (Micromeritics ASAP 2000 adsorption analyzer). The samples were previously degassed at 393 K for 8 h. Specific surface areas were calculated by the BET method.

Temperature-programmed ammonia desorption (TPD) experiments were performed to characterize the acidic properties of the pillared clays. In each TPD experiment, a sample weighing about 0.1 g was placed in the cell, which was evacuated at 673 K for 150 min and then cooled to 373 K. Ammonia gas of 65 Torr (1 Torr = 133.3 N m^{-2}) was adsorbed at 373 K for 15 min. After removing the weakly adsorbed ammonia by helium flow at 373 K for 1 h, the samples were heated at 10 K/min and the desorbed ammonia was recorded by a thermal conductivity detector (Intersmat IGC 120ML) and, in addition, was determined by the Kjeldhal method.

3. Results

XRD patterns of the sulfated titanium-modified pillared clays (SNTi-PILC and SHTi-PILC) dried at 523 K are presented in fig. 1. Each pattern exhibits two maxima. The first one is attributed to the layers intercalated by titanium polycations and the latter is due to layers not yet exchanged. The relative intensities of these lines are affected by both the SO_4^{2-}/Ti mole ratio and the sulfation procedure ($(NH_4)_2SO_4$ or H_2SO_4). Similar XRD pattern of the titanium pillared clay with respect to the sulfated titanium-modified pillared clays has been observed. Basal spacings corresponding to the first maximum are presented in table 1. As the SO_4^{2-}/Ti mole ratio increases, the lines corresponding to the pillared clays become less intense and the interlayer distances are reduced by more than 2 Å compared to the non-sulfated sample. As can be seen in table 1, the sulfation of Ti-PILC does not modify the X-ray pattern with respect to Ti-PILC.

The specific surface areas (A_{BET}) of the sulfated tita-

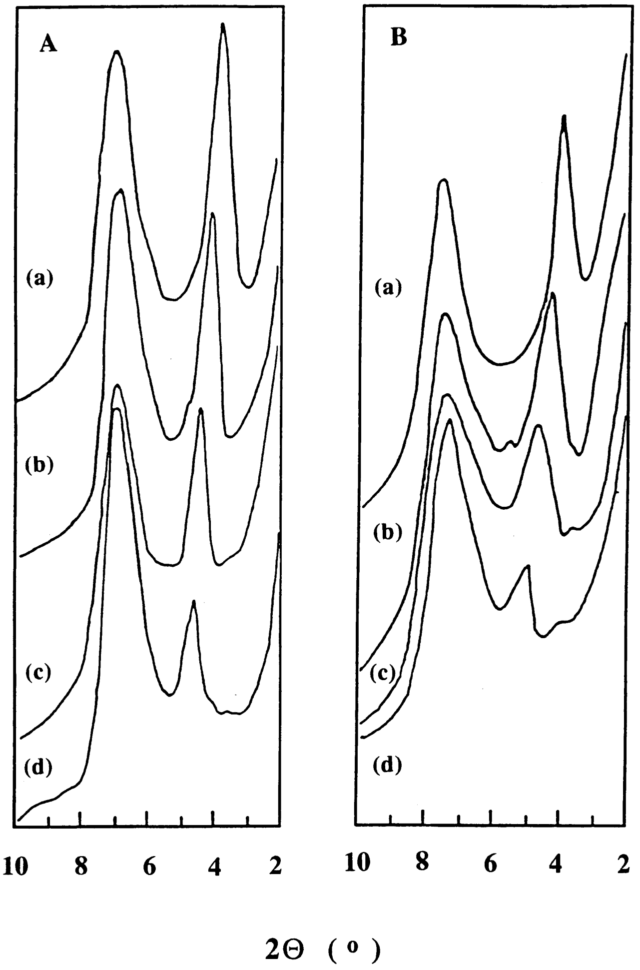

Fig. 1. X-ray diffraction patterns of the samples ((A) SNTi-PILC; (B) SHTi-PILC) as a function of the SO_4^{2-}/Ti mole ratio: (a) 0.025, (b) 0.075, (c) 0.25 and (d) 0.75.

nium-modified pillared clays (SNTi-PILC and SHTi-PILC) for a $SO_4^{2-}/Ti = 0.025$ mole ratio as a function of the temperature of calcination are presented in table 2. The specific surface areas for the Ti-PILC are also presented for comparison. The initial increase of specific surface area of the clay up to 336 $m^2\,g^{-1}$ in Ti-PILC is essentially related to the pillaring process. Increasing the temperature of calcination to 473 K increases the specific surface areas, but a further increase in the temperature of calcination causes a decrease in the specific surface area. This behaviour is related to an initial dehydration of both clays without loss of surface OH groups and a dehydroxylation of the clay and the titanium pillars along with the sintering of the titanium pillars. The three titanium pillared clays show the same behaviour and the specific surface areas decrease from Ti-PILC to SHTi-PILC.

The specific surface areas (A_{BET}) of the sulfated titanium-modified pillared clays as a function of the method of preparation, the temperature of calcination and the SO_4^{2-}/Ti mole ratio are presented in table 3. All the samples show a similar evolution. Thus, the specific surface areas of the SN(Ti-PILC) and SH(Ti-PILC) samples decrease as the SO_4^{2-}/Ti molar ratio or the temperature of calcination are increased. Therefore, SNTi-PILC and SHTi-PILC samples show higher specific surface areas than SN(Ti-PILC) and SH(Ti-PILC) samples, respectively.

The amount of NH_3 desorbed at 673 K as a function of the SO_4^{2-}/Ti mole ratio for the sulfated titanium-modified pillared clays are presented in table 4. The two series of sulfated titanium-modified pillared clays show a similar behaviour with the preparation method and the

Table 1
Basal spacings [$d(001)$] for the samples indicated (in Å)

Sample	SO_4^{2-}/Ti mole ratio				
	0	0.025	0.075	0.25	0.75
SNTi-PILC		22.0	21.4	20.0	19.0
SN(Ti-PILC)	22.5	22.4	22.2	22.1	22.0
SHTi-PILC		20.0	19.0	18.1	17.1
SH(Ti-PILC)	22.5	22.2	22.1	22.0	22.0

Table 2
Specific surface areas (BET method, in $m^2\,g^{-1}$) as a function of the calcination temperature. Sulfated titanium-modified pillared clays with a $SO_4^{2-}/Ti = 0.025$ mole ratio

Sample	Calcination temperature (K)				
	373	473	673	873	973
Ti-PILC	336	344	336	303	227
SNTi-PILC	294	305	294	240	214
SHTi-PILC	241	246	231	221	200

Table 3
Specific surface areas (BET method, in $m^2\,g^{-1}$) as a function of the calcination temperature, SO_4^{2-}/Ti mole ratio and the preparation method

Temperature (K)	SO_4^{2-}/Ti mole ratio			
	0.025	0.075	0.25	0.75
SNTi-PILC				
473	305	286	175	148
873	240	232	98	71
973	214	177	45	36
SN(Ti-PILC)				
473	244	229	89	123
873	214	195	65	48
973	173	136	32	18
SHTi-PILC				
473	246	227	191	160
873	221	209	87	64
973	200	164	44	32
SH(Ti-PILC)				
473	256	237	127	118
873	213	182	55	43
973	164	112	27	18

Table 4
Amount of NH_3 (μmol_{NH_3} m^{-2}) desorbed at 673 K as a function of the SO_4^{2-}/Ti mole ratio for the samples indicated

Sample	SO_4^{2-}/Ti mole ratio				
	0	0.025	0.075	0.25	0.75
Ti-PILC	1.48				
SNTi-PILC		2.09	2.17	4.54	5.58
SN(Ti-PILC)		2.69	2.76	3.10	2.55
SHTi-PILC		2.42	2.65	3.07	4.07
SH(Ti-PILC)		2.46	2.52	2.20	2.32

SO_4^{2-}/Ti mole ratio. For the two initial SO_4^{2-}/Ti mole ratios (0.025 and 0.075), the Ti-PILC sulfated samples (SN(Ti-PILC) and SNTi-PILC) present higher or similar (SH(Ti-PILC) and SHTi-PILC) amounts of NH_3 desorbed with respect of the titanium pillared clays intercalated with presence of SO_4^{2-}. As the SO_4^{2-}/Ti mole ratio increases (0.25 and 0.75), the titanium pillared clays synthesized in presence of SO_4^{2-} desorb a higher amount of NH_3 than the sulfated Ti-PILCs.

4. Discussion

When clays are intercalated with hydroxycations derived from a previous hydrolysis of metallic oxides or salts, these factors which can affect either the hydrolysis itself or the degree of polymerization are of major importance. For a given set of hydrolysis conditions, the polymerization of titanium depends on the nature of the anion in solution [2,38]. Therefore, in the hydrolysis of $TiCl_4$ with HCl, the presence of SO_4^{2-} can affect the average charge and size of the titanium polycation. In the same way, the competition of the polycation in the cation-exchange of the clay with NH_4^+, from $(NH_4)_2SO_4$, should be important during the process of intercalation. The evolution of the basal spacings of SNTi-PILC and SHTi-PILC with the SO_4^{2-}/Ti mole ratio (see table 1) can be related with the above cited phenomena. Our results also indicate that the presence of H_2SO_4 in the intercalation solution plays a more important role than the presence of $(NH_4)_2SO_4$. Farfan et al. [1] also used $(NH_4)_2SO_4$ to obtain sulfated Zr-PILC. It was shown that the influence of the SO_4^{2-}/Zr mole ratio on the basal spacings is very important, this being also related with the polymeric species formed. These results were in agreement with the CEC values presented by these authors [1]. The differences in basal spacings observed in this work when Ti-PILC is obtained by hydrolysis of $TiCl_4$ with HCl or H_2SO_4 can also be related with the nature of the polymeric species [2].

Clearfield et al. [3] and Molinard et al. [39] observed that the treatment with various concentrations of HCl and NaOH modify the textural properties of an Al-PILC. An increase of the specific surface area was observed when the Al-PILC is treated with HCl [39]. These authors explained this behaviour by the partial dissolution of the pillars by HCl. In the case of the NaOH treatment, the opposite behaviour was observed, and a small partial breakdown of the structure and/or some pore blocking due to the formation of $Al(OH)_3$ was proposed. Taking into account that our conditions of sulfation do not affect the structure of the clay [24,26,34], a partial dissolution of the titanium polycations, before calcination, could explain the gradual reduction of the basal spacing in SN(Ti-PILC) and SH(Ti-PILC) as the SO_4^{2-}/Ti mole ratio increases. This sulfation procedure also affects the textural properties. The decrease in basal spacings obtained for SNTi-PILC and SHTi-PILC ($SO_4^{2-}/Ti = 0.025$ mole ratio, table 1) are also confirmed by a decrease in the specific surface area (table 2) with respect to Ti-PILC. In the light of the present results, it is possible to indicate that the presence of $(NH_4)_2SO_4$ and H_2SO_4 in the intercalation solution affects the pillaring process. The resulting properties can also be affected by a partial pore blocking due to the presence of sulfated groups in the pores. The evolution of the specific surface areas with the calcination temperature (table 2) indicates that the textural properties remain stable at high temperature treatment, 200 m^2 g^{-1} for the three samples.

The evolution of the specific surface area with the SO_4^{2-}/Ti mole ratio and the temperature of calcination for the two series of samples (table 3) also gives evidence for the competition of the polycation with NH_4^+ in the cation-exchange of the clay, as well as for the influence of SO_4^{2-} on the size of the titanium polycation and its partial dissolution. These results (table 3) also indicate that upon sulfation, the surface of the montmorillonite was not affected. Modifications in the textural properties by acid treatments of various silicates have been reported in the literature [21,40]. Studies with montmorillonites have shown that this silicate is only affected when it is treated under aggressive conditions [24,40], giving rise to an increase of the specific surface areas, which was explained by the presence of amorphous silica.

Finally, as can be seen in table 4, an initial increase of the acidity for the $SO_4^{2-}/Ti = 0.025$ mole ratio can be observed for the sulfated titanium-modified pillared clays, when compared with the non sulfated pillared clay [41]. The total acidity only increases with the SO_4^{2-}/Ti mole ratio when $(NH_4)_2SO_4$ or H_2SO_4 are present in the solution of intercalation (SNTi-PILC and SHTi-PILC). Therefore, the most important acidity sites do not result from the post-treatment of the Ti-PILC by impregnation.

For titanium pillared clays, an initial increase of the Lewis acidity can be related to the interaction between the titanium oxide pillar and the silicate layer [8]. This hypothesis seems likely since bulk TiO_2 does not evidence this acid character. The structure of the catalytically active species responsible for giving highly acidic properties has been related with an organic sulfate structure [42]. This sulfite-like structure shows two covalent S=O bonds and the highly acidic properties are related with the dynamic transformation of the structure. In the same way, Khalfallah Boudali et al. [2] observed, with a similar procedure of preparation, that the sulfation of Ti-PILC enhances the Brønsted acidity. These new acid centers were also evidenced by catalytic tests [40]. Nevertheless, the presence of $(NH_4)_2SO_4$ or H_2SO_4 in the solution of intercalation makes that the sulfate ions should issue from the titanium polymers and remain in the pillared clay. This also suggests that they are initially enclosed in the structure of the polymers thus explaining the enhancement of acidity.

5. Conclusions

The results presented in this work show that sulfated titanium-modified pillared clays can be obtained with high surface areas and acidity. These results also indicated that the agents of sulfation and the methods affect the properties of the final titanium-modified pillared clay. The presence of $(NH_4)_2SO_4$ or H_2SO_4 in the solution of intercalation reduces the interlayer distances, with respect to the non-sulfated sample. Nevertheless, the specific surface areas remain high and an important enhancement of acidity is obtained. These properties have been related with the presence of the sulfate ions in the structure of the titanium polymers.

Acknowledgement

AG wishes to thank Dr. L.M. Gandía for critical reading of the manuscript. The financial support of the SPPS (Service de Programmation de la Politique Scientifique), Belgium, is gratefully acknowledged.

References

[1] E.M. Farfan-Torres and P. Grange, in: *Catalytic Science and Technology*, eds. S. Yoshida, N. Takezawa and T. Ono (Kodansha/Elsevier, Tokyo/Amsterdam, 1991) p. 103.
[2] L. Khalfallah Boudali, A. Ghorbel, D. Tichit, B. Chiche, R. Dutartre and F. Figueras, Microporous Mater. 2 (1994) 525.
[3] A. Clearfield, H.M. Aly, R.A. Cahill, G.P.D. Serrette, W.-L. Shea and T.-Y. Tsai, in: *Studies in Surface Science and Catalysis*, Vol. 83, eds. T. Hattori and T. Yashima (Kodansha/Elsevier, Tokyo/Amsterdam, 1993) p. 433.
[4] F. Bouchet, H. Fujisawa, M. Kato and T. Yamaguchi, in: *Studies in Surface Science and Catalysis*, Vol. 84, eds. J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Elsevier, Amsterdam, 1994) p. 2029.
[5] M. Barrer and D.M. MacLeod, Trans. Faraday Soc. 51 (1955) 1290.
[6] D.E.W. Vaughan, P.K. Maher and E.W. Albers, US Patent 3,775,345 (1973).
[7] D. Tichit, F. Fajula, F. Figueras, C. Gueguen and J. Bousquet, in: *ACS Symp. Series*, 375, ed. M.L. Ocelli (Am. Chem. Soc., Washington, 1988) p. 237.
[8] H.L. del Castillo and P. Grange, Appl. Catal. A 103 (1993) 23.
[9] J.P. Sterte, Clays Clay Minerals 34 (1986) 658.
[10] A. Bernier, L.F. Admaiai and P. Grange, Appl. Catal. 77 (1991) 269.
[11] S. Yamanaka, T. Nishihara and M. Hattori, Mater. Chem. Phys. 17 (1987) 87.
[12] S.-J. Jong, J.-T. Lin and S. Chung, in: *Studies in Surface Science and Catalysis*, Vol. 83, eds. T. Hattori and T. Yashima (Kodansha/Elsevier, Tokyo/Amsterdam, 1993) p. 33.
[13] T. Kijima, H. Nakazawa and S. Takenouchi, Bull. Chem. Soc. Jpn. 64 (1991) 1395.
[14] M.L. Occelli, Catal. Today 2 (1988) 339.
[15] M.L. Occelli and R.M. Tindwa, Clays Clay Minerals 31 (1983) 22.
[16] M.-Y. He, Z. Lin and E. Min, Catal. Today 2 (1988) 321.
[17] Y.F. Shen, A.N. Ko and P. Grange, Appl. Catal. 67 (1990) 93.
[18] T. Yamaguchi, Appl. Catal. 61 (1990) 1.
[19] C.N. Rhodes and D.R. Brown, J. Chem. Soc. Faraday Trans. 89 (1993) 1387.
[20] C.R. Theocharis, K.J. s'Jacob and A.C. Gray, J. Chem. Soc. Faraday Trans. I 84 (1988) 1506.
[21] M.A. Vicente, J. de D. López and M.A. Bañares, Microporous Mater. 4 (1995) 251.
[22] I.E. Odon, Soc. Mineral. Eng. AIME Trans. 282 (1988) 1893.
[23] D.R. Taylor and D.B. Jenkins, Soc. Mineral. Eng. AIME Trans. 282 (1988) 1901.
[24] R. Mokaya, W. Jones, M.E. Davis and M.E. Whittle, J. Mater. Chem. 3 (1993) 381.
[25] M. Zyla and M. Olzzar, Mineral. Pol. 15 (1984) 67.
[26] S. Mendioroz, J.A. Pajares, I. Benito, C. Pesquera, F. Gonzalez and C. Blanco, Langmuir 3 (1987) 676.
[27] F. Figueras, Catal. Rev. Sci. Eng. 30 (1988) 457.
[28] W. Jones, Catal. Today 2 (1988) 357.
[29] S.M. Bradley and R.A. Kydd, J. Catal. 141 (1993) 239.
[30] H. Auer and H. Hofmann, Appl. Catal. A 97 (1993) 23.
[31] D. Plee, F. Borg, L. Gatineau and J.J. Fripiat, J. Am. Chem. Soc. 107 (1985) 2362.
[32] S. Bodardo, F. Figueras and E. Garrone, J. Catal. 147 (1994) 223.
[33] L. Zhougui and S. Guida, in: *Zeolites*, eds. B. Drzaj, S. Hovecar and S. Pejovnik (Elsevier, Amsterdam, 1985) p. 493.
[34] Z. Ge, D. Li and T.J. Pinnavaia, Microporous Mater. 3 (1994) 165.
[35] D.T.B. Tennakon, W. Jones and J.M. Thomas, J. Chem. Soc. Faraday Trans I 82 (1986) 3081.
[36] A. Shutz and G. Poncelet, in: *Proc. of the NATO Workshop on Chemical Reactions in Organic and Inorganic Systems* (Reidel, Dordrecht, 1985).
[37] J.P. Chen, M.C. Hausladen and R.T. Yang, J. Catal. 151 (1995) 135.
[38] J. Livage, M. Henry and C. Sanchez, Progr. Solid State Chem. 18 (1988) 259.
[39] A. Molinard, A. Clearfield, H.Y. Zhu and E.F. Vansant, Microporous Mater. 3 (1994) 109.
[40] C. Pesquera, F. Gonzalez, I. Benito, C. Blanco, S. Mendioroz and J.A. Pajares, J. Mater. Chem. 2 (1992) 907.
[41] H.L. del Castillo, A. Gil and P. Grange, Catal. Lett. 36 (1996) 237.
[42] O. Saur, M. Bensitel, A.B.M. Saad, J.C. Lavalley and B.M. Morrow, J. Catal. 99 (1986) 104.