Dehydrogenation of ethylbenzene on alumina–chromia-pillared saponites

M.A. Vicente [a,*], A. Meyer [b], E. González [b], M.A. Bañares-Muñoz [a], L.M. Gandía [c], and A. Gil [c]

[a] *Departamento de Química Inorgánica, Universidad de Salamanca, Plaza de la Merced s/n, 37008-Salamanca, Spain*
[b] *Departamento de Química, Facultad de Ciencias, Universidad del Zulia, Apartado 526, Maracaibo, Venezuela*
[c] *Departamento de Química Aplicada, Universidad Pública de Navarra, Campus de Arrosadía, 31006-Pamplona, Spain*

Received 5 June 2001; accepted 26 September 2001

A natural saponite was intercalated and pillared with hydroxy-aluminium–chromium oligomers. The intercalation solutions were characterized by visible spectroscopy and the pillared saponites mainly by chemical analyses, X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and nitrogen adsorption. The catalytic behaviour of these materials in the dehydrogenation of ethylbenzene was investigated. The selectivity to styrene was found to increase as the chromium content of the pillared clays decreased.

KEY WORDS: alumina–chromia-pillared saponite; pillared clays; ethylbenzene dehydrogenation

1. Introduction

Pillared interlayered clays constitute a group of microporous materials widely studied in recent years. These solids are obtained by calcination of the intercalated compounds prepared by exchange of the interlayer cations of layered clays with bulk inorganic oligomers. The oligomers, mainly synthesized by partial hydrolysis of multivalent cations, such as Al^{3+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, Ga^{3+}, Si^{4+} or Fe^{3+}, among others, are inserted between the clay layers and, after calcination, yield stable *pillars* that permanently prop apart the layers preventing its collapse. The pillars may be described, in a first approximation, as oxide-like phases, although due to the interaction with the clay layers, they are somewhat different from bulk oxides. Thus, the pillared clays can also be regarded as nanocomposites, in which oxide particles of nano- and subnanometer scales are incorporated into the interlayer space of the clay. An alternative way of describing these materials is by indicating that the clay layers stabilize the pillar particles thus avoiding their aggregation. Pillaring creates a new porous structure and new active sites are also incorporated, making these solids promising adsorptive and catalytic materials [1–7].

The aim of this work is to report our preliminary results on the styrene selectivity yielded by some pillared saponites in the gas-phase ethylbenzene dehydrogenation reaction. The main route to the commercial production of styrene, an important chemical used for the production of styrene polymers and copolymers, is the catalytic dehydrogenation of ethylbenzene at high temperature (873–973 K) [8]. Many catalysts which mainly consist of Fe and K oxides containing one or more promoters (Mg, Ce, Cr, Mo, V, Ca), and acid solids such as zeolites and metal phosphates have been employed for this reaction as a result of a constant search to improve catalysts and reaction conditions [9,10]. In this paper, we investigate the potential of a saponite intercalated with hydroxy-aluminium–chromium polycations as a catalyst for this reaction.

2. Experimental

The starting material used in this work was a natural saponite from the Yunclillos deposit (Toledo province, Spain), supplied by TOLSA S.A., Madrid, Spain. The particle size fraction below 2 μm was obtained by careful aqueous decantation of the raw material. Some small amounts of quartz and feldspars were detected by X-ray diffraction. Taking into account these impurities, the following structural formula of the saponite on the basis of 22 oxygen atoms, was found: $[Si_{7.42}Al_{0.58}][Mg_{5.16}Fe_{0.14}Al_{0.26}Mn_{0.004}Ti_{0.02}]$ $O_{20}(OH)_4[Mg_{0.24}Ca_{0.124}Na_{0.020}K_{0.084}]$. Its cation-exchange capacity (CEC) was 1.15 meq/g, and its specific surface area was very large, 161 m^2/g, because of the very small particle size owing to the sedimentary origin of the deposit.

Four hydroxy-aluminium–chromium solutions were prepared by slow addition of a 1 M NaOH solution to solutions of aluminium and chromium ($AlCl_3{\cdot}6H_2O$ (Panreac, P.A.) and $Cr(NO_3)_3{\cdot}9H_2O$ (Panreac, P.A.)), with Al^{3+}/Cr^{3+} ratios of 0.8/0.2, 0.5/0.5, 0.2/0.8 and 0.1/0.9 and aged at room temperature. In all cases, a $OH^-/(Al^{3+} + Cr^{3+})$ mole ratio equal to 2.2 and a pH of 4.1 were established.

Pillared clays were obtained by slow addition of the solutions over suspensions of 8 g of saponite with an $(Al^{3+} + Cr^{3+})$ concentration in the final suspensions of 0.03 mol/dm^3 and a metal/clay ratio of 5.0 mmol/g. The solids were kept in contact with the solution at room temperature for 24 h, washed by centrifugation and dialysis until the absence of

---

[*] To whom correspondence should be addressed. E-mail: mavicente@gugu.usal.es

chloride and nitrate, dried at 323 K for 16 h and calcined in a furnace. The samples were referred to as YUsap-$Al_{0.8}Cr_{0.2}$, YUsap-$Al_{0.5}Cr_{0.5}$, YUsap-$Al_{0.2}Cr_{0.8}$ and YUsap-$Al_{0.1}Cr_{0.9}$, respectively.

Intercalating aluminium–chromium solutions were studied by visible spectroscopy using a Hewlett–Packard HP 8452A spectrophotometer. Diffuse reflectance spectra of the intercalated and pillared solids in this series were recorded on a Shimadzu UV-240 spectrophotometer, using 5 nm slits and MgO as reference.

X-ray diffraction (XRD) patterns of the solids in the powder form were obtained by using a Siemens D-500 diffractometer, at 40 kV and 30 mA (1200 W) and employing Cu Kα filtered radiation. The equipment was connected to a DACO-MP microprocessor and used Diffract-AT software.

Elemental analyses of the solids were carried out by Activation Laboratories Ltd., Ancaster, Ontario, Canada, using inductively coupled plasma spectroscopy (ICPS) and atomic absorption spectroscopy (AAS).

The specific surface areas were measured by N_2 (SCO, 99.9992%) adsorption at 77 K using a static automatic volumetric apparatus (Micromeritics ASAP 2010 adsorption analyzer). Samples were previously degassed at 383 K for 8 h.

Ethylbenzene dehydrogenation was carried out in a tubular fixed-bed glass reactor at atmospheric pressure. The reactor feed consisted of a nitrogen stream saturated with ethylbenzene (1 vol%). Ethylbenzene dehydrogenation reaction was performed at 673 K and W/Q ratio of 6.67×10^{-3} $g_{cat.}$ min/cm^3. On-line analysis of the product stream was performed on a Perkin–Elmer Autosystem XL gas chromatograph equipped with a Carbowax 20M column connected to a FID for hydrocarbon analyses. Selectivities were defined as the mole fraction of the reacted ethylbenzene that was converted into a given product.

3. Results and discussion

Aluminium and chromium polyoxocation species are known to exist in base-hydrolyzed solutions of Al^{3+} and Cr^{3+} cations. When the hydroxide to aluminium mole ratio (OH^-/Al^{3+}) is 2.0–2.2, Al^{3+} mainly polymerizes as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, abbreviated Al_{13}, a modified-Keggin aluminium ion [11]. In the case of chromium, Cr^{3+} forms the dimer $[Cr_2(OH)_2(H_2O)_8]^{4+}$ or the trimer $[Cr_3(OH)_4(H_2O)_9]^{5+}$, or does not polymerize, remaining as $[Cr(H_2O)_6]^{3+}$. The visible spectrum and the extinction coefficients can qualitatively characterize the polymerization degree of the chromium species [12]. When the intercalating solutions were made up of a mixture of Al^{3+} and Cr^{3+} cations, the formation of the polycations was conditioned by the competitive bonding of Al^{3+} and Cr^{3+} cations to the OH^- added to the solutions [12]. Al^{3+} polymerized first, and the Cr species formed depended on the amount of OH^- remaining when all the Al^{3+} was polymerized. Thus, when the Al/Cr ratio was high, there were many Al^{3+} cations that consumed all the OH^- during their polymerization, avoiding the polymerization of Cr^{3+} cations; when the Al/Cr ratio was low, the low amount of Al^{3+} consumed only a few OH^-, and the Cr-trimer was formed. When intermediate ratios were used, the Cr-dimer was formed.

The basal spacings corresponding to the maxima of the XRD patterns of the intercalated clays are summarized in table 1; these values ranged between 18.0 and 19.9 Å. Considering the minimum layer width of saponite (9.8 Å after calcination at 773 K), the length of the polycations in the interlayer space varied from 8.2 to 10.1 Å, which agreed both with the intercalation of Al_{13} and the different Cr-oligomers [11,13,14] and also with a mixed pillar as Dubbin and Goh [15] have recently proposed from ^{27}Al MAS NMR analysis. The evolution with temperature of the basal spacings depended on the Al/Cr ratio used. When Cr^{3+} was the main intercalating cation (YUsap-$Al_{0.1}Cr_{0.9}$), the resulting values were 16.9 Å at 473 K and 12.0 Å at 573 K. The basal spacings increased as the amount of Al^{3+} in the intercalating solutions also increased. The XRD patterns of YUsap-$Al_{0.5}Cr_{0.5}$ as a representative pillared solid of these series are shown in figure 1.

The results of the chemical analysis are also included in table 1. The amounts of aluminium and chromium fixed by the intercalated solids also depended on the Al/Cr ratios used; up to 8.60% Al_2O_3 and 11.72% of Cr_2O_3 were fixed, taking into account the chemical composition of the starting saponite (YUsap). These amounts were equivalent to 0.11 Al_{13} pillars and 0.478 Cr_3 units per $[O_{20}(OH)_4]$ saponite unit cell. Whereas the Al fixation was equivalent to a high pillar density of about one Al_{13} unit per 9 unit cells, the maximum density permitted by steric constraints has been calculated to be one Al_{13} unit per 5.9 unit cells [16,17]. Obviously, for

Table 1
Physicochemical properties and chemical analyses (wt%) of the alumina–chromia-pillared saponites

Sample	$d(001)^a$ (Å)	S_{BET}^b (m^2/g)	SiO_2	Al_2O_3	K_2O	Fe_2O_3	MgO	Cr_2O_3
YUsap	14.9	161	61.33	5.64	0.62	1.44	29.29	–
YUsap-$Al_{0.8}Cr_{0.2}$	19.0	224	54.52	14.24	0.53	1.36	24.25	4.79
YUsap-$Al_{0.5}Cr_{0.5}$	19.5	369	54.46	9.33	0.55	1.35	24.14	9.84
YUsap-$Al_{0.2}Cr_{0.8}$	19.9	310	54.52	6.86	0.51	1.37	24.76	11.68
YUsap-$Al_{0.1}Cr_{0.9}$	18.0	242	55.52	6.29	0.55	1.36	24.23	11.72

[a] Samples dried at 323 K.
[b] Samples degassed at 383 K.

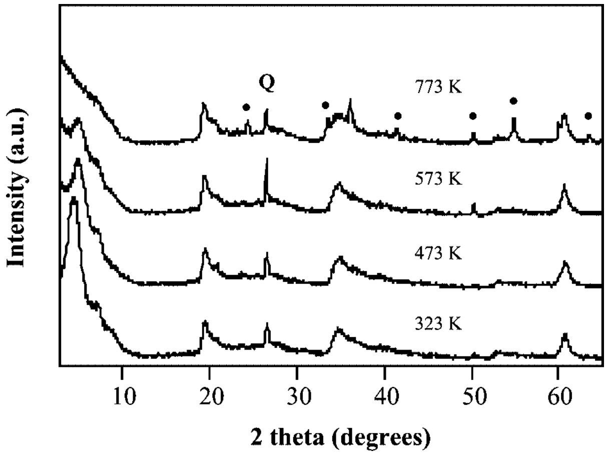

Figure 1. XRD patterns of the YUsap-$Al_{0.5}Cr_{0.5}$ series treated at various temperatures. Positions of quartz (Q) and Cr_2O_3 (●) reflection peaks are indicated.

the various series, as the amount of Cr fixed increased, the amount of Al decreased, and *vice versa*. Accordingly the same trend was followed by the number of pillars of each element. The comparison of the results for the SiO_2, K_2O, Fe_2O_3 and MgO contents between YUsap and the pillared saponites indicated that the intercalation process did not produce any significant deleterious effect on the clay structure.

The BET specific surface areas of the intercalated clays, treated at 383 K, reached a maximum for YUsap-$Al_{0.5}Cr_{0.5}$ as the Cr fixed increased (see table 1). The evolution of the specific surface area when calcining the intercalated solids to obtain the pillared ones was rather different for each series. When Al^{3+} was the majority cation in the intercalating solutions, the solids calcined at 773 K maintained about 80% of the specific surface area of the corresponding intercalated materials. When Cr^{3+} was the majority cation in the intercalating solutions, the solids calcined at 473 K maintained almost the same surface area as the intercalated ones (237–314 m^2/g), and at 573 K the specific surface area strongly decreased (165–180 m^2/g) to values similar to that of the natural saponite. The YUsap-$Al_{0.5}Cr_{0.5}$ series showed an intermediate behaviour: 332 m^2/g for the solid treated at 473 K, 301 m^2/g at 573 K, and 181 m^2/g for the solid calcined at 773 K. Thus, it can be concluded that the incorporation of chromium produced a decrease in the thermal stability of the pillared solids in comparison with their alumina-pillared counterparts. Finally, it must be mentioned that upon calcination at high temperature, Cr^{3+} polycations led to a Cr_2O_3 eskolaite phase [12,18], detectable by XRD (see figure 1), DRS and by DTA-TGA analyses under air atmosphere. The presence of chromium species with a higher oxidation state could not be detected from these techniques.

The overall ethylbenzene conversions reached a constant value lower than 10% after 30 min on-stream. The reaction products detected by gas chromatography were styrene and benzene, which resulted from the dehydrogenation and the cracking of ethylbenzene, respectively. The evolution with time-on-stream of the selectivities to the reaction products yielded by the various catalysts is shown in figures 2 and 3. The results suggest that a relation exists between the amount of chromium present in the solids and the selectivity of the reaction. Initially, the solids with high chromium content (YUsap-$Al_{0.1}Cr_{0.9}$ and YUsap-$Al_{0.2}Cr_{0.8}$) showed a high cracking activity that rapidly decreased, indicating a fast deactivation of the active sites for this reaction. Simultaneously, the dehydrogenation activity increased with time-on-stream of reaction. It seems that the nature of the pillars is important in determining the specific catalytic behavior of the pillared clays used in this work.

It has been reported that cracking and dehydrogenation activities may be related to the presence of Brønsted and Lewis acid sites [19–21]. The intercalation and pillaring processes of layered clays generate new acid sites (whose nature is still not well known) on the resulting solids [22]. The acidity and acid site type (Brønsted and

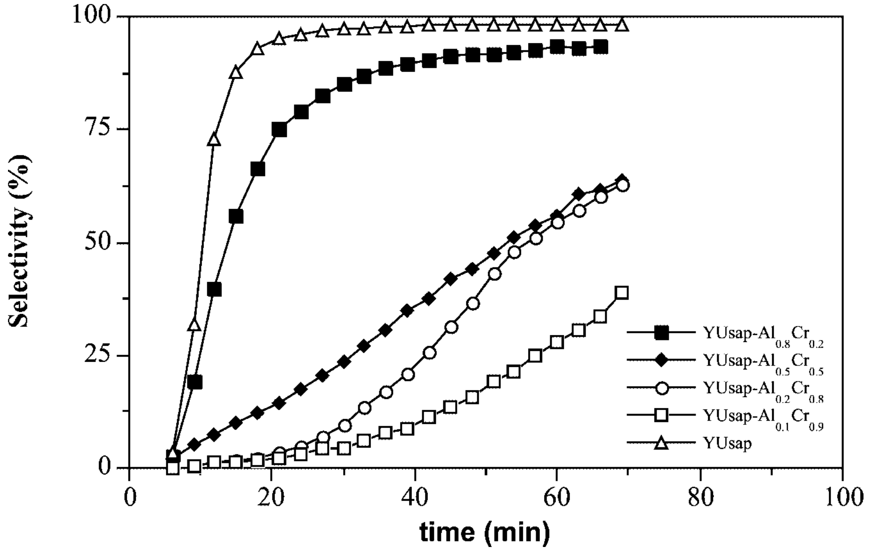

Figure 2. Evolution of the selectivity to styrene with time-on-stream for the conversion of ethylbenzene at 673 K over the catalysts indicated.

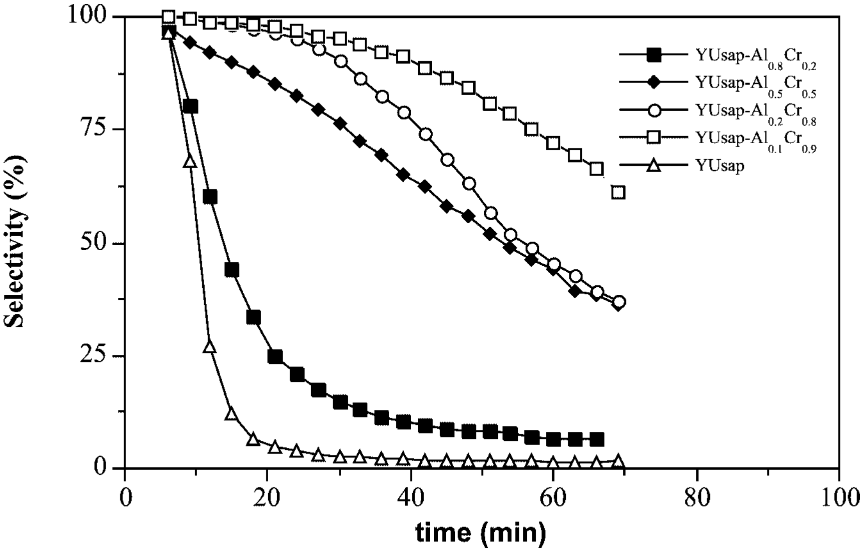

Figure 3. Evolution of the selectivity to benzene with time-on-stream for the conversion of ethylbenzene at 673 K over the catalysts indicated.

Lewis) depend on the exchanged cations [1,19,23], the preparation method [1,19,23,24], and the nature of the starting clay [25–27]. It is well known that Lewis acidity in alumina pillared clays is related to two types of aluminium sites [28]: aluminium sites in the layers of the clay and aluminium sites on the pillars. The second ones are currently regarded as of the Lewis type. On the other hand, the origin and the location of Brønsted acid sites in pillared clays are still not clear. Several sources for Brønsted acidity have been discussed in the literature: (i) the structural hydroxyl groups in the clay layers from the initial sites of ion exchange [23,25,29,30]; (ii) the protons derived from the cationic oligomers which, upon heating, decompose into metal oxide pillars and liberate protons [19,24]; (iii) a synergy phenomenon between the siliceous clay sheet and the pillar [28,31,32]. These general considerations about the acid properties of pillared clays may be consistent with the results found for the ethylbenzene conversion.

To further investigate the Brønsted and Lewis acidity of pillared clays, the cumene and decane conversion were chosen by various authors as model reactions [19,21,33]. These authors studied the influence of the chromium present on pillared clays for these reactions. Although the effect of the chromium on the ratio of the cracking to the dehydrogenation activities was not explained, it was suggested that it might be related to the acidity. Cañizares *et al.* [34] and Zhao *et al.* [35] obtained an increase of the total acidity measured by TPD of ammonia when a bentonite was intercalated and pillared with hydroxy-aluminium–chromium oligomers. These results were related to the intrinsic acidity of chromium. Our results can be explained if the presence of chromium contributes to a higher Brønsted acidity in a similar way, as Jamis *et al.* proposed previously [36]. If so, the increase in cracking activity accords with the presence of more Brønsted acid sites as the chromium content of the catalyst increases. As a result, the styrene selectivity for the ethylbenzene conversion over the alumina–chromia-pillared saponites increases in the order YUsap-$\mathrm{Al}_{0.1}\mathrm{Cr}_{0.9}$ < YUsap-$\mathrm{Al}_{0.2}\mathrm{Cr}_{0.8}$ < YUsap-$\mathrm{Al}_{0.5}\mathrm{Cr}_{0.5}$ < YUsap-$\mathrm{Al}_{0.8}\mathrm{Cr}_{0.2}$.

4. Conclusions

Intercalation and pillaring of a saponite with hydroxy-aluminium–chromium oligomers resulted in an increase of the interlayer spacing, thus increasing the specific surface areas and further exposing Brønsted and Lewis acid sites. The pillars contribute to the acidic character and the catalytic behaviour in a different way for the different Al/Cr ratios used. The results of the ethylbenzene conversion revealed that the unpillared saponite as well as saponites with alumina-rich pillars exhibited almost exclusively dehydrogenation activity, whereas the presence of chromia induced cracking activity and reduced the selectivity to styrene.

Acknowledgment

MAV and MABM are grateful for the financial support of the Comisión Interministerial de Ciencia y Tecnología, CICYT (ref. MAT99-0956) and Junta de Castilla y León (ref. SA26/00B). The authors also thank the Spain–France project *Acción Integrada Hispano Francesa* ref. HF2001-0106 (Ministerio de Ciencia y Tecnología (Spain) and Ministère des Affaires Étrangères (France)).

References

[1] F. Figueras, Catal. Rev. Sci. Eng. 30 (1988) 457.
[2] A. Clearfield, in: *Advances in Catalysts and Nanostructured Materials. Modern Synthetic Methods*, ed. W.R. Moser (Academic Press, San Diego, 1996) p. 345.
[3] J.F. Lambert and G. Poncelet, Topics Catal. 4 (1997) 43.
[4] K. Othsuka, Chem. Mater. 9 (1997) 2039.

[5] P. Cool and E.F. Vansant, in: *Molecular Sieves-Science and Technology*, Vol. 1, Synthesis, eds. H.G. Karge and J. Weitkamp (Springer, Berlin, 1998) p. 265.
[6] J.T. Kloprogge, J. Porous Mater. 5 (1998) 5.
[7] A. Gil, L.M. Gandía and M.A. Vicente, Catal. Rev. Sci. Eng. 42 (2000) 145.
[8] C. Hagopian, in: *Kirk–Othmer, Encyclopedia of Chemical Technology*, 3th Ed., Vol. 21, eds. J. Brown, C.I. Eastman, C. Golojuch, A. Klingsberg and M. Wainwright (Wiley, New York, 1982) pp. 770–801.
[9] K. Tanabe, M. Misono, Y. Ono and H. Hattori, in: *New Solid Acids and Bases. Their Catalytic Properties*, Vol. 51, Stud. Surf. Sci. Catal. (Elsevier, Amsterdam, 1989) pp. 316–320.
[10] F. Cavani and F. Trifirò, Appl. Catal. A 133 (1995) 219.
[11] S.M. Bradley, R.A. Kydd and R. Yamdagni, J. Chem. Soc. Dalton Trans. (1990) 2653.
[12] R. Toranzo, M.A. Vicente and M.A. Bañares-Muñoz, Chem. Mater. 9 (1997) 1829.
[13] C. Volzone, A.M. Cesio, R.M. Torres Sánchez and E. Pereira, Clays Clay Miner. 41 (1993) 702.
[14] G.W. Brindley and S. Yamanaka, Am. Miner. 64 (1979) 830.
[15] W.E. Dubbin and T.B. Goh, Clay Miner. 32 (1997) 485.
[16] L. Bergaoui, J.F. Lambert, R. Franck, H. Suquet and J.L. Robert, J. Chem. Soc. Faraday Trans. 91 (1995) 2229.
[17] L. Bergaoui, J.F. Lambert, M.A. Vicente-Rodríguez, L.J. Michot and F. Villiéras, Langmuir 11 (1995) 2849.
[18] M.A. Vicente, R. Toranzo, M.A. Bañares-Muñoz and E. Rodríguez, An. Quím. Int. Ed. 94 (1998) 136.
[19] S.M. Bradley and R.A. Kydd, J. Catal. 141 (1993) 239.
[20] T. Mishra and K. Parida, Appl. Catal. A 166 (1998) 123.
[21] S. Vijayakumar, C. Vijaka, K. Rengaraj and B. Sivasankar, Bull. Chem. Soc. Jpn. 67 (1994) 3107.
[22] H.L. del Castillo, A. Gil and P. Grange, Catal. Lett. 43 (1997) 133.
[23] M.-Y. He, Z. Lin and E. Min, Catal. Today 2 (1988) 321.
[24] H. Auer and H. Hofmann, Appl. Catal. A 97 (1993) 23.
[25] D. Plee, F. Borg, L. Gatineau and J.J. Fripiat, J. Am. Chem. Soc. 107 (1985) 2362.
[26] R. Molina, A. Schutz and G. Poncelet, J. Catal. 145 (1994) 79.
[27] R. Molina, S. Moreno, A. Vieira-Coelho, J.A. Martens, P.A. Jacobs and G. Poncelet, J. Catal. 148 (1994) 304.
[28] S. Bodoardo, F. Figueras and E. Garrone, J. Catal. 147 (1994) 223.
[29] D.T.B. Tennakon, W. Jones and J.M. Thomas, J. Chem. Soc. Faraday Trans. I 82 (1986) 3081.
[30] A. Schutz and G. Poncelet, in: *Proc. NATO Workshop on Chemical Reactions in Organic and Inorganic Systems*, ed. R. Setton (Reidel, Dordrecht, 1986) p. 165.
[31] M.L. Occelli and R.M. Tindwa, Clays Clay Miner. 31 (1983) 22.
[32] J.P. Chen, M.C. Hausladen and R.T. Yang, J. Catal. 151 (1995) 135.
[33] K.A. Carrado, S.L. Suib, N.D. Skoularikis and R.W. Coughlin, Inorg. Chem. 25 (1986) 4217.
[34] P. Cañizares, J.L. Valverde, M.R. Sun Kou and C.B. Molina, Micropor. Mesopor. Mater. 29 (1999) 267.
[35] D. Zhao, Y. Yang and X. Guo, Zeolites 15 (1995) 58.
[36] J. Jamis, A. Drljaca, L. Spiccia and T.D. Smith, Chem. Mater. 7 (1995) 2078.