

Characterization of Mo/Al₂O₃ sol–gel catalyst by ²⁷Al nuclear magnetic resonance spectroscopy

Ihl Hyun Cho ^a, Seung Bin Park ^{a,*}, Ja Hun Kwak ^b

^a Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Taejon 305-701, South Korea

^b Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, South Korea

Received 10 January 1995; accepted 29 June 1995

Abstract

The Mo/Al₂O₃ catalysts at various molybdenum loading was prepared by adding (CH₃COCH=C(O–)CH₃)₂MoO₂ (Mo-acac), dissolved in ethanol, to the boehmite alumina sol driven from aluminum isopropoxide (AIP). The structural evolution of Mo/Al₂O₃ gel was investigated by using ²⁷Al nuclear magnetic resonance (NMR) spectroscopy and X-ray diffractometry (XRD). ²⁷Al NMR of Mo/Al₂O₃ has been compared with that of pure alumina. The addition of molybdenum species to alumina sol was to have no effect on the alumina structure when the molybdenum loading was lower than 20%. No incorporation of molybdenum species to alumina lattice was observed and the finely dispersed MoS₂ crystallite on the support was obtained upon sulfidation. However, an Al₂(MoO₄)₃ phase, which was an indication of the interaction between Al₂O₃ and MoO₃, was formed on the alumina surface when molybdenum loading was higher than 20%. All molybdenum species were accessible by reactant molecules regardless of molybdenum loading.

Keywords: ²⁷Al NMR; Sol–gel; Hydrodesulfurization; Alumina; Molybdenum; Aluminum molybdate

1. Introduction

The sol–gel processing [1] has been a popular subject in ceramic's research due to its inherent advantages such as molecular level mixing, low vitrification temperature, and facile control of composition. Possibility of applying the sol–gel processing to the preparation of impregnated catalyst was proposed and tested [2–6]. The sol–gel processing of catalyst involves hydrolysis of the precursor for support and addition of the active metal species at the due steps. In this process, the primary concern is to know the location, dispersion, and morphology of the active components.

Gomez et al. prepared sol–gel catalysts by adding metals, such as, Pt, Pd and Ru, before gelation [2–4]. They reported that part of the metal (M = Pt, Pd, Ru) was incorporated into the silica network as Si–O–M or was formed into emerged particles, which lead to metal–support interactions that were different from those of conventionally impregnated catalysts.

The alumina framework was reported to be modified by the incorporation of molybdenum in sol–gel catalysts when the molybdenum precursor was mixed with the aluminum alkoxide before hydrolysis [5]. When the molybdenum precursor was mixed with alumina sol, fine crystallites of molybdenum oxide are deposited on the alumina

* Corresponding author.

surface without modifying the alumina framework [6].

In this paper, Mo/Al₂O₃ catalysts were prepared by adding (CH₃COCH=C(O–)CH₃)₂MoO₂ (Mo-acac) to the alumina sol. The effect of molybdenum precursor addition on the structural change of alumina sol, gel, and final calcined sample was investigated by X-ray diffractometry (XRD) and ²⁷Al NMR (nuclear magnetic resonance) technique, which has been used for investigating the environment of the aluminum atoms during hydrolysis and gelation of aluminum alkoxide [7–10]. Thiophene hydrodesulfurization (HDS) activity at various molybdenum loadings was also reported.

2. Experimental

The preparation procedure of the Mo/Al₂O₃ catalysts by sol–gel method following Yoldas [11,12] was shown in Fig. 1. First, aluminum isopropoxide (AIP; Junsei, 99%) was hydrolyzed at 85°C for 30 min with water to an AIP mole ratio of 100. This solution was then peptized by adding HNO₃ (Junsei; HNO₃/AIP=0.2 mol ratio) and transparent sol of aluminum monohydroxide

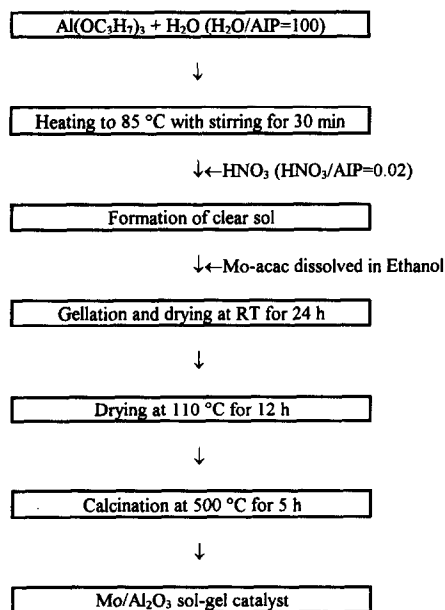


Fig. 1. Preparation procedure of Mo/Al₂O₃ sol–gel catalyst.

[5,11,12] was obtained. After the peptized sol was stirred at 85°C for 12 h, Mo-acac (Aldrich), dissolved in ethanol, was mixed with this transparent alumina sol. The resulting green solution was stirred vigorously at 85°C for 1 h and dried at room temperature for 24 h and subsequently at 110°C for 12 h. The dried gel was calcined at 500°C for 5 h under air flow, followed by sulfidation with 10 mol% H₂S/H₂ mixture (200 ml min⁻¹) at 400°C for 2 h. The Mo/Al₂O₃ gel was white and turned into black upon sulfidation. A series of Mo/Al₂O₃ samples, with 11, 20, 28, 35 and 41% loading based on Al₂O₃, was prepared. Pure alumina without adding Mo precursor was also prepared by the same procedure.

The solid state ²⁷Al NMR was obtained at 296 K using a Bruker AM-300 FT-NMR spectrometer with magic angle spinning (MAS) units. Operating frequency of ²⁷Al was 78.2 MHz, and the sample was spun at 3.5 kHz. The spectrum was obtained with 100–200 acquisitions repeated with 2-s recycle delay and 3-μs pulse width (30° pulse angle). The chemical shift was referenced with respect to the ²⁷Al signal of (Al(H₂O)₆)³⁺. All the ²⁷Al NMR spectra were directly obtained for freshly prepared samples without hydration treatment. XRD patterns were collected using a Rigaku D/MAX-RB equipped with CuKα X-ray source. TEM micrographs were obtained using a Philips Model CM20. The TEM samples were prepared by dispersing the ground catalyst in ethanol and then dropping a drop of the dispersed catalyst on a copper grid coated by carbon film.

Thiophene HDS reaction were conducted in a packed-bed reactor with 1 mol% C₄H₄S/H₂ (250 ml min⁻¹) under atmospheric pressure. The amount of catalyst was fixed at 0.25 gram and the bed temperature was set at 400°C. The reactants and products were analyzed by an on-line HP 5840A GC with a flame ionized detector (FID).

3. Results and discussion

3.1. ²⁷Al NMR spectra of alumina

Fig. 2 shows the ²⁷Al NMR spectra of alumina sol after heat treatment. The typical spectrum of

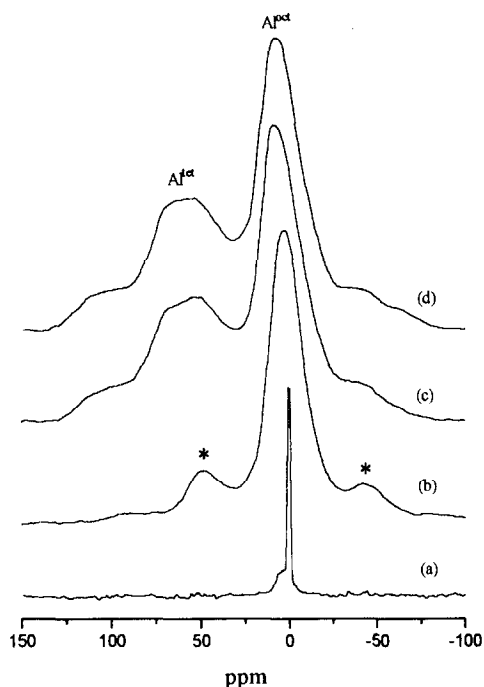


Fig. 2. ^{27}Al NMR spectra of alumina prepared by sol-gel method: (a) alumina sol; (b) dried at 110°C ; (c) calcined at 300°C ; (d) calcined at 500°C . Al^{tet} and Al^{oct} denote the tetrahedrally and octahedrally coordinated aluminum, respectively. Spinning side bands are marked by asterisks.

alumina sol, Fig. 2a, was consistent with other reports that gave a resonance peak near 0 ppm [7,8]. The ^{27}Al chemical shift is governed primarily by the coordination number of aluminum atoms. The chemical shift for octahedral aluminum varies in the range of 0–20 ppm relative to $(\text{Al}(\text{H}_2\text{O})_6)^{3+}$ whereas the chemical shift for tetrahedral aluminum is within 50–80 ppm relative to the same reference [13]. According Fig. 2a, there are almost no tetrahedral aluminum atoms in the alumina sol. The ^{27}Al NMR spectrum obtained right after peptization was identical to the one obtained 8 h after peptization. Electrostatic attraction and repulsions inhibit the agglomeration, thus a stable sol is maintained during peptization process.

Fig. 2b shows the solid-state ^{27}Al NMR spectrum of alumina gel dried at 110°C . The spectrum was broader than that of alumina sol, and only one resonance at 4 ppm was observed. It indicates that there is no phase transformation during the drying of alumina sol. The small peaks on both sides of

the main resonance peak were spinning side bands. However, heat treatment of the alumina gel at 300°C induced marked changes in the ^{27}Al NMR spectrum as shown in Fig. 2c. Dwivedi and Gowda [14] obtain the same result. Some octahedral Al was transformed to tetrahedral Al showing resonance at 53 ppm. The ^{27}Al NMR spectrum of alumina gel after heat treatment at 500°C (Fig. 2d) was very similar to the spectrum of γ -alumina. XRD also revealed the formation of γ - Al_2O_3 from the AIP-derived gel heated at 500°C (Fig. 4a).

3.2. ^{27}Al NMR and XRD spectra of a series of $\text{Mo}/\text{Al}_2\text{O}_3$

Fig. 3 shows ^{27}Al NMR spectra on a series of $\text{Mo}/\text{Al}_2\text{O}_3$ gels after being calcined at 500°C . The ^{27}Al NMR spectrum of $\text{Mo}/\text{Al}_2\text{O}_3$ gel at Mo loading $\leq 20\%$ was almost same as that of alumina gel. When the MoO_3 loading was greater than 20%, the $\text{Al}_2(\text{MoO}_4)_3$ phase which appeared at -14 ppm [15] was observed and the amount of this phase was increased with Mo loading. But the

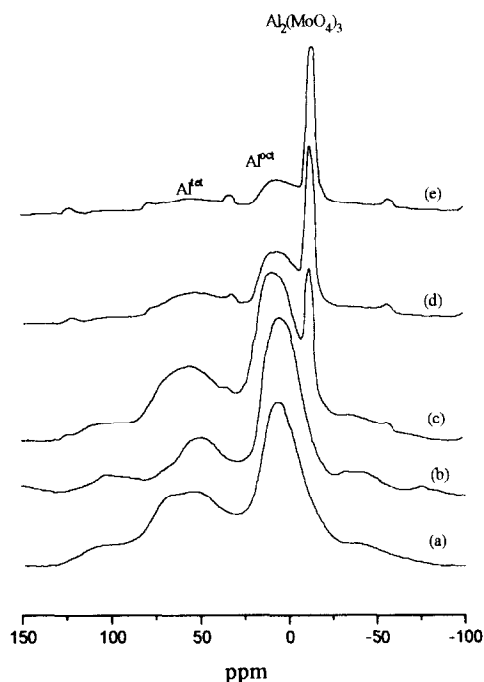


Fig. 3. ^{27}Al NMR spectra of $\text{Mo}/\text{Al}_2\text{O}_3$ gel calcined at 500°C : (a) alumina gel; (b) 20%; (c) 28%; (d) 35%; (e) 41%.

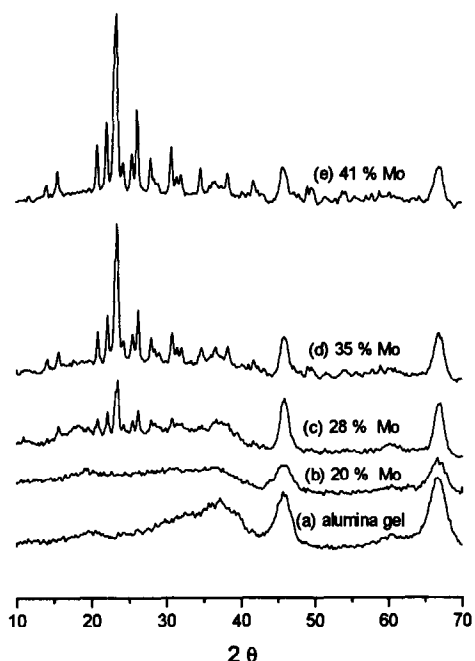


Fig. 4. XRD patterns of Mo/Al₂O₃ after being calcined at 500°C: (a) alumina gel; (b) 20%; (c) 28%; (d) 35%; (e) 41%.

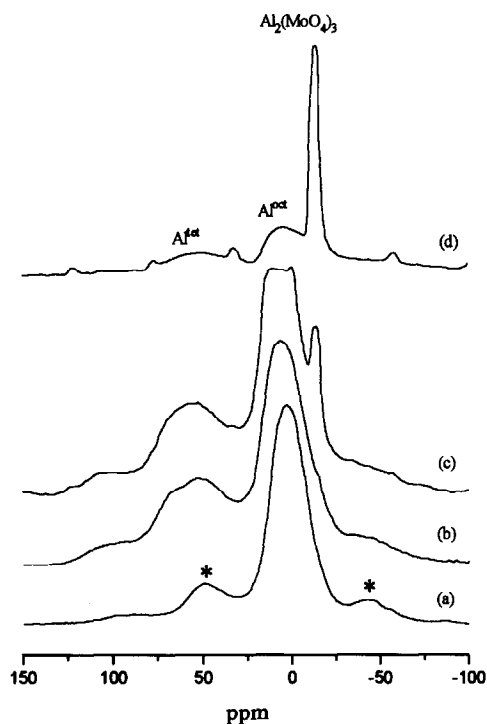


Fig. 5. ²⁷Al NMR spectra of 41% Mo/Al₂O₃ with various heat treatments: (a) dried at 110°C; (b) 300°C; (c) calcined at 500°C for 1 h; (d) 500°C for 5 h.

other peaks were remained unchanged. XRD peaks, shown in Fig. 4, are consistent with the NMR result. Al₂(MoO₄)₃ peaks appeared above 20% molybdenum loading.

Fig. 5 shows the changes of solid state ²⁷Al NMR spectrum of 41% Mo/Al₂O₃. When the samples were calcined above 500°C, Al₂(MoO₄)₃ phase appeared and the amount of this phase increased with calcination time (Fig. 5c and d). These results indicate that the interaction between γ-Al₂O₃ and MoO₃ is significant when molybdenum loading is higher than 20%.

Fig. 6 shows XRD patterns of Mo/Al₂O₃ gel before and after sulfidation process. The aluminum molybdate phase disappeared with sulfidation treatment. This observation suggests that the Al₂(MoO₄)₃ phase is present on the surface of alumina and reacts easily with H₂S.

From these results, we can conclude that, when the molybdenum loading lower than 20%, molybdenum species are distributed over the alumina gel structure without being incorporated into the alumina network, but when the loading is over 20%, the Al₂(MoO₄)₃ compound is formed on the outside surface of alumina gel.

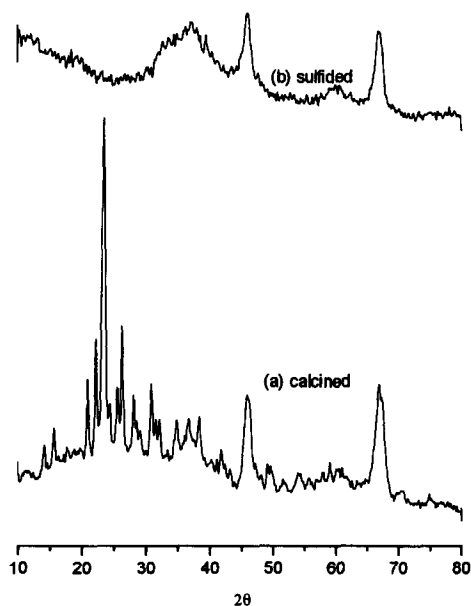


Fig. 6. XRD patterns of 35% Mo/Al₂O₃: (a) calcined at 500°C; (b) sulfided at 400°C.

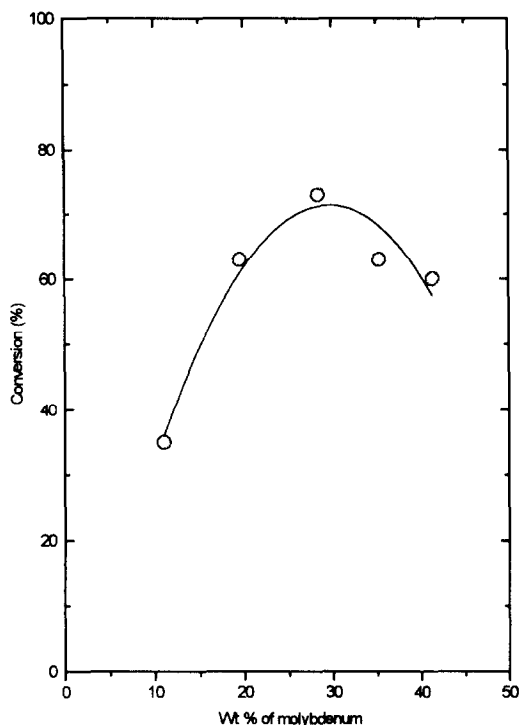


Fig. 7. Thiophene conversion as a function of molybdenum loading.

3.3. HDS activity of the sol–gel catalyst

The thiophene conversion as a function of molybdenum loading is shown in Fig. 7. The conversion increases at molybdenum loadings up to 30%. For a conventionally impregnated Mo/Al₂O₃ catalyst, the maximum activity is known to be present at 12–15% molybdenum loading which is the limit of monolayer formation of molybdenum in the surface of alumina [16]. In contrast to the impregnated catalyst, for the sol–gel catalysts, HDS activity did not decrease at molybdenum loading higher than 15%. It should be noted that the conversion was doubled as the loading was increased from 11% to 20%. This is an important result indicating that most of the Mo atoms are accessible by the reactants.

Fig. 8 shows a typical TEM micrograph of the sulfided Mo/Al₂O₃ gel. It contains groups of black parallel lines which are from crystalline sheets of MoS₂ in a highly dispersed form. The highly dispersed form of MoS₂ are known to be contributed to the high level of the thiophene HDS activity for Mo/Al₂O₃ catalysts [17]. The structure of MoS₂

slabs using TEM has been investigated by other researchers [18–20].

The structure of the oxidic precursor of MoS₂ phase can be described as an oligomeric species of molybdenum which is formed in an early stage. When (CH₃COCH=C(O–)CH₃)₂MoO₂ dissolved in ethanol is added to the alumina sol, it is expected that molybdenum species become oligomeric clusters resulting from the partial hydrolysis and polymerization of Mo-acac. The oligomeric clusters, after sulfidation process, could be evolved to be partially sulfided clusters and eventually reduced to an MoS₂ slab [18].

The decrease of thiophene conversion for Mo/Al₂O₃ at molybdenum loading above 30% can be explained by the sharp decrease of surface area as shown in Table 1. The BET surface area of Mo/Al₂O₃ gel below 20% molybdenum loading was in the range 150–200 m² g^{–1}, which was larger than that of pure alumina gel (152 m² g^{–1}). However, the BET surface areas of Mo/Al₂O₃ gel with 41 wt.-% MoO₃ loading were 43 m² g^{–1}. The pronounced decrease of surface area is likely to be due to the pore blocking of the Mo species. Thus, the thiophene conversion was decreased as the molybdenum loading increased.

4. Conclusions

The Mo/Al₂O₃ catalyst was prepared by adding Mo-acac to the alumina sol obtained by the Yoldas procedure [11,12] and characterized with ²⁷Al NMR, XRD, TEM, and the thiophene HDS reaction. All Mo active phase was found to be exposed

Table 1
BET surface area of pure alumina and Mo/Al₂O₃ sol–gel catalysts

Samples	BET surface area (m ² g ^{–1})
Alumina ^a	152
11% Mo/Al ₂ O ₃ ^a	192
20% Mo/Al ₂ O ₃ ^a	189
41% Mo/Al ₂ O ₃ ^b	71
41% Mo/Al ₂ O ₃ ^a	40

^a Calcined at 500°C for 5 h.

^b Calcined at 500°C for 1 h.

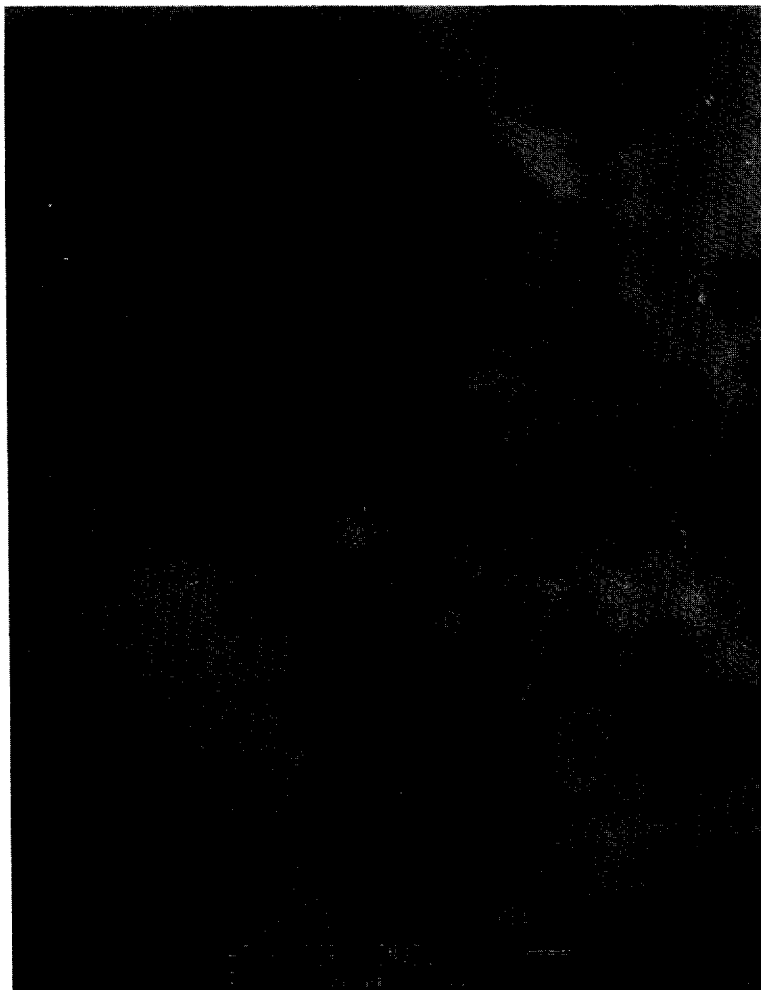


Fig. 8. TEM microscopy of sulfided Mo/Al₂O₃ sol-gel catalysts.

on the surface of alumina and thus was accessible by the reactants. After sulfidation, molybdenum particles were transformed into finely dispersed MoS₂ crystallites which were the active phase for HDS reaction. The Al₂(MoO₄)₃ phase began appear for Mo/Al₂O₃ at molybdenum loading higher than 20%. The Al₂(MoO₄)₃ phase exists on the surface of alumina as surface compound and thus it is converted to the sulfided form upon sulfidation

Acknowledgements

We thank Prof. R. Ryoo for his helpful discussion. This work was supported by the Research

Center for Catalytic Technology (RCCT), Pohang University of Science and Technology.

References

- [1] C.J. Brinker and G.W. Scherer, Sol-Gel Science, Academic Press, Orlando, FL, 1990.
- [2] P. Bosch, T. Lopez, V. H. Lara and R. Gomez, J. Mol. Catal., 80 (1993) 299.
- [3] T. Lopez, A. Romero and R. Gomez, J. Non-Cryst. Solids, 127 (1991) 105.
- [4] T. Lopez, P. Bosch, M. Asomoza and R. Gomez, J. Catal., 133 (1992) 247.
- [5] E. Etienne, E. Ponthieu, E. Payen and J. Grimblot, J. Non-Cryst. Solids, 147/148 (1992) 764.
- [6] K. Ishiguro, T. Ishikawa, N. Kakuta, A. Ueno, Y. Mitarai and T. Kamo, J. Catal., 123 (1990) 523.

- [7] W.L. Olson and L.J. Bauer, in *Better Ceramics Through Chemistry II*, Mater. Res. Soc. Symp. Proc., 73 (1986) 187.
- [8] L.F. Nazar and L.C. Klein, *J. Am. Ceram. Soc.*, 71 (1988) C85.
- [9] T. Assih, A. Ayril, M. Abenoza and J. Phalippou, *J. Mater. Sci.*, 23 (1988) 3326.
- [10] S. Komarneni, R. Roy, C. Fyfe and G.J. Kennedy, *J. Am. Ceram. Soc.*, 68 (1985) C243.
- [11] B.E. Yoldas, *Am. Ceram. Soc. Bull.*, 54 (1975) 286.
- [12] B.E. Yoldas, *J. Mater. Sci.*, 10 (1975) 1856.
- [13] G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicalites and Zeolite*, Wiley, New York, 1987.
- [14] R.K. Dwivedi and G. Gowda, *J. Mater. Sci. Lett.*, 4 (1985) 331.
- [15] G.W. Haddix, M. Narayana, S.C. Tang and Y. Wu, *J. Phys. Chem.*, 97 (1993) 4624.
- [16] K.V.R. Chary, H. Ramakrishna and G. Murali Dhar, *J. Mol. Catal.*, 68 (1991) L25.
- [17] E. Diemann, T. Weber and A.M. Iler, *J. Catal.*, 148 (1994) 288.
- [18] M. de Boer, A.J. van Dillen, D.C. Koningsberger and J.W. Geus, *J. Phys. Chem.*, 98 (1994) 7862.
- [19] J.V. Sanders and K.C. Pratt, *J. Catal.* 67 (1981) 331.
- [20] F.D. Delannay, P. Gajardo, P. Grange and B. Delmin, *J. Chem. Soc. Faraday 1*, 76 (1980) 988.