

Tailored mesoporous alumina prepared from different aluminum alkoxide precursors

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Abstract The importance of aluminum alkoxides precursors (ethoxide, isopropoxide and *sec*-butoxide) in the tailoring of the structural and textural properties of γ -alumina was reported. It has been found that the specific surface areas (336–426 m²/g), as well as the mean pore size distribution are modified in function of the length and branching of the aluminium alkoxide used in the synthesis. A narrow pore size distribution was obtained with aluminum ethoxide (14.7 nm), meanwhile a broad pore size distribution was observed in samples prepared with aluminium *sec*-butoxide or aluminium isopropoxide precursors (18.2 and 19.4 nm). In fresh samples, Boehmite phase and Al^{VI} octahedrally coordinated were identified by XRD and ²⁷Al MAS-NMR spectroscopies. After annealing at 500°C, the samples showed the γ -alumina phase formation and a mixture of aluminium in tetrahedral Al^{IV} and octahedral Al^{VI} coordination in variable proportions. The acidity of the calcined samples, determined from the pyridine-FTIR spectra, showed Lewis and Brønsted type acidity. Activity in the 2-propanol dehydration reaction showed that the highest activity corresponds to the samples showing the highest Lewis acidity.

Keywords Alumina · Ethoxide · Sol-gel · Boehmite · Alkoxide

1 Introduction

The extensive use of alumina as catalyst support, justifies the research of new techniques of synthesis, in order to improve the properties of these materials. One suitable route in the preparation of alumina is the sol-gel method, since it has been reported that with this method it is possible to tailoring the physical and catalytic properties of the alumina [1–3]. During the sol-gel process, the involved reactions are the hydrolysis of the precursors and the condensation of hydrolyzed alkoxides. The alumina used as support in catalytic reactions requires in most of the cases a high specific surface area and controlled pore size distribution [4]. In the sol-gel synthesis of alumina the more frequently precursors used were aluminium isopropoxide or aluminium *sec*-butoxide hydrolyzed preferentially in a large excess of water and in the presence of an acid catalyst [1–7]. However, it has been reported few studies with short alkoxy groups as precursors, such as aluminum ethoxide or a mixture of them.

Because of the interest of the control of the textural and structural properties of aluminas, for their use as industrial catalytic supports, in the present work the preparation of alumina using three different aluminum alkoxides: ethoxide, isopropoxide, *sec*-butoxide, and ethoxide mixed with *sec*-butoxide is reported. The present work includes the preparation and characterization of sol-gel alumina by means of N₂ adsorption, X-ray diffraction (XRD), pyridine-FTIR adsorption, ²⁷Al MAS NMR spectroscopy techniques, and the

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determination of the catalytic properties using the 2-propanol dehydration as catalytic test.

2 Experimental section

The preparation method used was the sol-gel route. First, the alcohol (ethanol, *sec*-butanol or 2-propanol) was put in a glass flask at 25 °C and then the aluminum precursor (ethoxide, isopropoxide, *sec*-butoxide or a stoichiometric mixture of them) was added. Then, the corresponding amount of water was added to this solution, drop by drop (under constant stirring). The solution was kept under stirring at 70 °C for 30 min. After the gel was formed, the sample was dried at 120 °C for 24 h and subsequently thermally treated at 500 ° or 750 °C in air. The alcohol/alkoxide mole ratio was 10 (in order to obtain an optimum dispersion of the components) and the water/alkoxide mole ratio was 4 (to obtain a complete hydrolysis during the reaction). The alcohols and alkoxides used in the different synthesis are reported in Table 1.

The specific surface areas and the mean pore size diameter were determined by nitrogen adsorption using a Micromeritics ASAP 2000 apparatus. The specific surface areas were calculated from the corresponding nitrogen adsorption isotherms using the BET method and the mean pore size diameter and distribution was calculated using the BJH method. The types of acid sites (Brønsted or Lewis) were evaluated by pyridine adsorption with a Fourier Transform Infrared (FTIR) Nicolet 170 SX spectrometer in the temperature desorption range 50–500 °C. Before pyridine adsorption, the samples were heated under vacuum to 300 °C, and then cooled to room temperature. Afterwards, the solid wafer was exposed to pyridine for 20 min by breaking, inside the spectrometer cell, a capillary tube containing liquid pyridine. The IR spectra were recorded at various temperatures by heating the cell from 50 to 500 °C under vacuum.

X-ray diffraction patterns were obtained with a Siemens D-5000 diffractometer. A Cu target was used as X-ray source (Cu K α , $\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. The diffraction peaks of the samples were

recorded for diffraction angles from 5 to 80° with a step time of 2s and a step size of 0.02° (2θ).

^{27}Al MAS NMR spectra of the solids were recorded in a 300 MHz Bruker spectrometer. A 4.5- μs pulse (90°) was used with a repetition time of 5s between pulses in order to avoid saturation effects. The spinner frequency of the zirconia cylindrical sample was kept within the 4–4.5 kHz range. The number of signal accumulations was 500. All measurements were carried out at room temperature with $\text{Al}(\text{H}_2\text{O})_6^{3+}$ as standard reference for aluminum.

The catalytic activity of the alumina samples calcined at 500 °C was determined in a fixed bed reactor at low conversion and atmospheric pressure. 2-propanol was passed through the reactor by means of a saturator using nitrogen as carrier gas. The partial pressure of the alcohol in the feed was 22.4 Torr and the reaction temperature was 150 °C. The products were analysed in a gas chromatograph apparatus coupled to the reaction system. The only products detected were propene and acetone.

3 Results and discussion

The specific surface areas and the mean pores size of the different samples are reported in Table 2. The samples calcined at 500 °C showed large specific areas between 336 and 426 m²/g. The highest BET specific surface area corresponds to the sample prepared with the mixture of aluminum ethoxide and aluminum *sec*-butoxide precursors.

The pore size distributions of the alumina samples (calcined at 500 °C) are shown in Fig. 1. The aluminas synthesized with aluminum ethoxide had narrow pore size distributions (samples C and AC), meanwhile for the *sec*-butoxide (sample A) and the isopropoxide (sample B) samples almost a bimodal pore size distribution was obtained. These results showed that it is possible to control the pore size diameter and its distribution by varying the aluminum alkoxide precursors: large pores can be obtained using larger alkoxy groups

Table 1 Alkoxides and alcohols used in the preparation of sol-gel alumina

Sample	aluminum alkoxide	Alcohol
A	<i>sec</i> -butoxide	<i>sec</i> -butanol
B	isopropoxide	2-propanol
C	ethoxide	ethanol
AC	<i>sec</i> -butoxide and ethoxide	<i>sec</i> -butanol and ethanol

Table 2 Textural properties of the sol-gel aluminas

Sample	Calcined at 500 °C		Calcined at 750 °C	
	Specific area (m ² /g)	Pore diameter nm	Specific area (m ² /g)	Pore diameter nm
A	336	18.2	207	25.4
B	419	19.4	249	25.2
C	382	14.7	266	18.1
AC	426	14.6	265	18.4

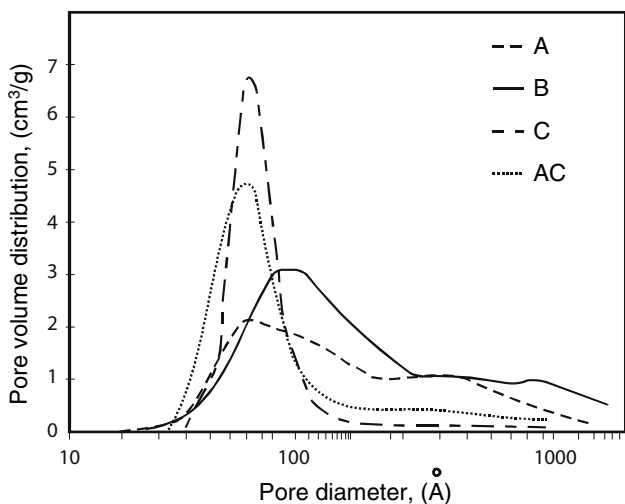


Fig. 1 Pore volume distribution of sol-gel aluminas calcined at 500 °C

and small ones when shorter alkoxy groups are used for the sol-gel synthesis.

In order to study the stability of the supports prepared by the sol-gel method the samples were sintered at 750 °C for 4 h in air, and the results are reported in Table 2. It can be seen that, in general, the specific surface areas diminish at higher annealing temperatures, meanwhile they were compressed between 254 and 181 m²/g (being solids with acceptable sintering resistance). The adsorption–desorption isotherms of the calcined samples (500 °C) are shown in Fig. 2. All the isotherms are type IV, which characterizes mesoporous materials. The hysteresis loop for the A and B samples corresponds to the H3 type [8]. The adsorption-desorption cycle of the H3 type is characteristic of

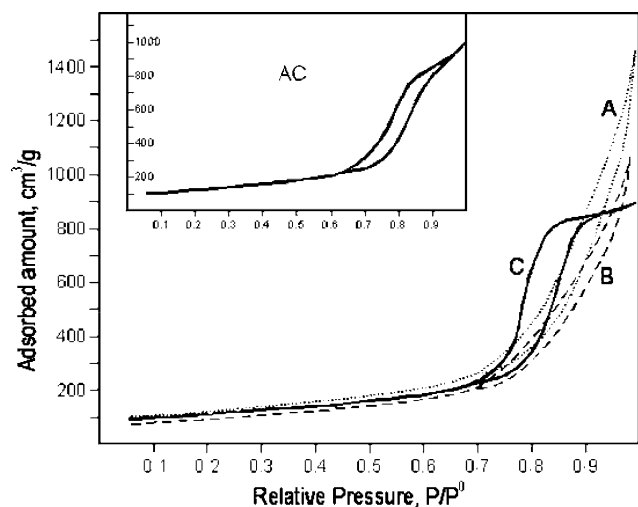


Fig. 2 The adsorption–desorption isotherms of sol-gel aluminas calcined at 500 °C

particle aggregates in form of plates, which gives to slit-shaped pores (the plates are characteristic of commercial aluminas). The alumina prepared with ethoxide precursor (Fig. 2) shows a cycle of hysteresis of the H1 type. This type of H1 hysteresis is associated with porous of agglomerates with a compact packing of spheres (close-packed structure), which has narrow pore size distributions [8]. The hysteresis loop of alumina prepared from the ethoxide precursor showed that this alumina does not form multilayers. These results indicate that the preparation procedure is crucial for obtaining specific textural properties, leading to the formation of two types of pores. On the other hand, the sample prepared with the mixture of two alkoxides, (sample AC), presented a cycle of hysteresis that looks like a hybrid of the H1 and H3 types. In this sample (alumina AC) a different shape of pore was formed if it is compared with the ethoxide and *sec*-butoxide preparations.

The powder X-ray diffraction patterns (XRD) of the fresh samples prepared with the different aluminum alkoxides are shown in Fig. 3. In all samples the peaks correspond to the Boehmite crystalline phase [9]. Boehmite exhibits a lamellar structure within an orthorhombic symmetry. Each layer constitutes the (OAlOH–HOAlO) stacking sequence [10]. The octa-

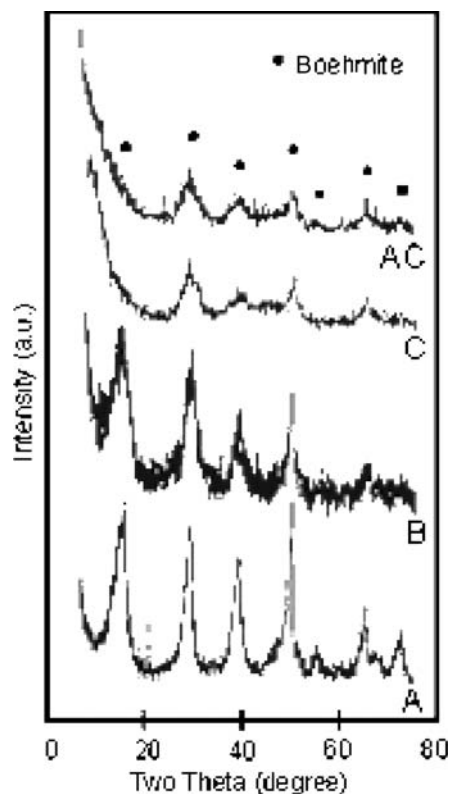


Fig. 3 X-ray diffraction patterns of fresh sol-gel aluminas

hedral aluminum is surrounded by four tetrahedral oxygens and two hydroxyl groups. The cohesion of the stacked layers is ensured by hydrogen bonds between hydroxyl groups belonging to two consecutive layers and forming a zigzag chain [10]. An important detail in the XRD patterns is shown in the fresh sample prepared with aluminum ethoxide, because in this sample the peak between 0–20 two theta does not appear. The peak in this position corresponds to the inter-planar distance between the Boehmite layers [11] and it means that the fresh sample from the ethoxide precursor does not have this kind of layers, moreover, a similar XRD pattern was obtained for the AC sample. In calcined samples the corresponding XRD patterns (Fig. 4) showed amorphous alumina (Fig. 4) and the positions of the peaks correspond to γ -alumina [9].

^{27}Al MAS-NMR spectra of the samples were obtained from fresh and calcined samples. The resonance position is reported between 55 and 70 ppm for tetrahedral aluminum Al^{IV} , around 25–30 ppm for the pentacoordinated aluminum Al^{V} , and at 0–11 ppm for the octahedrally coordinated Al^{VI} [12–15]. It can be seen in Fig. 5 that the octahedral aluminum is formed in the fresh samples and not big differences are observed in the peaks (octahedral aluminum forms the Boehmite phase [10]). Meanwhile, when the samples

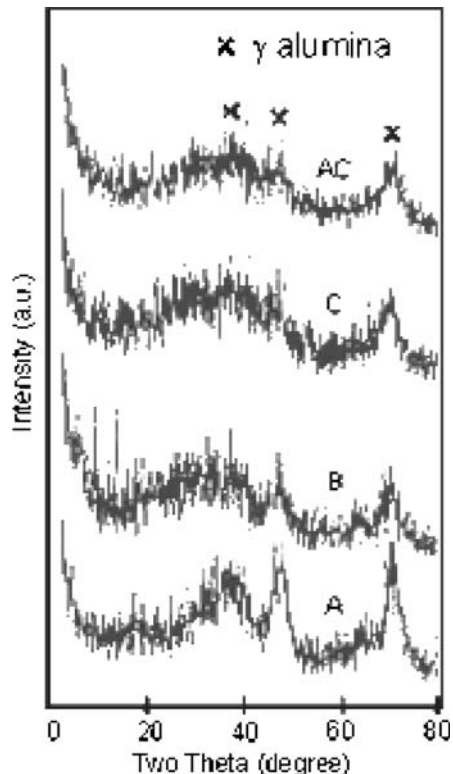


Fig. 4 X-ray diffraction patterns of sol-gel aluminas calcined at 500 °C

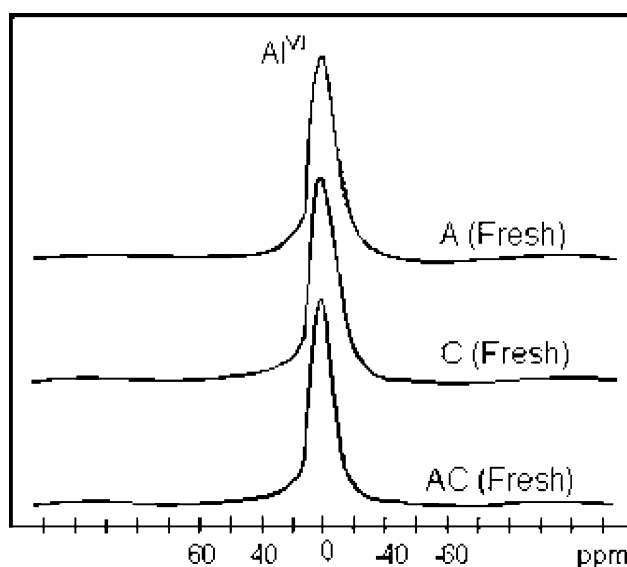


Fig. 5 ^{27}Al MAS NMR spectra of fresh sol-gel aluminas samples

were calcined at 500 °C, octahedral and tetrahedral aluminum was observed (Fig. 6). The effect of the aluminium precursor in structural properties of the alumina can be observed, since in the analysis of the Fig. 6, it can be seen that the sample prepared with aluminum *sec*-butoxide showed a relative highest abundance of tetrahedral aluminum when comparing with the other preparations.

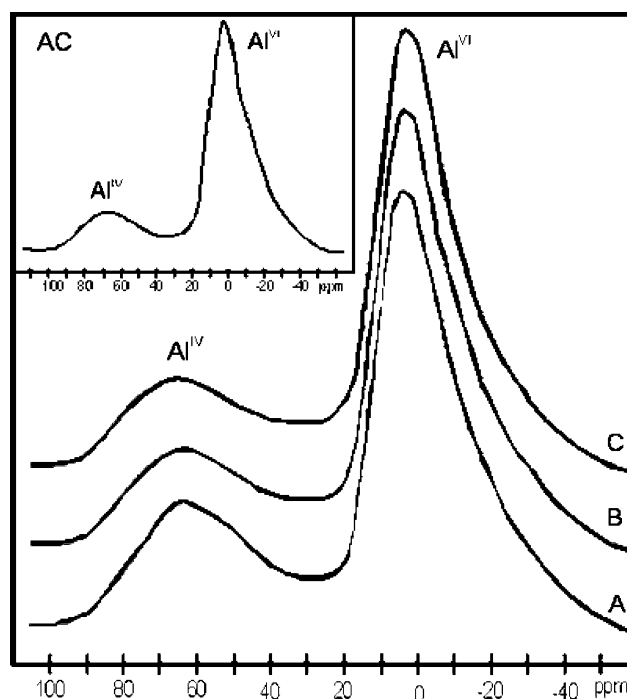


Fig. 6 ^{27}Al MAS-NMR spectra of sol-gel aluminas calcined at 500 °C

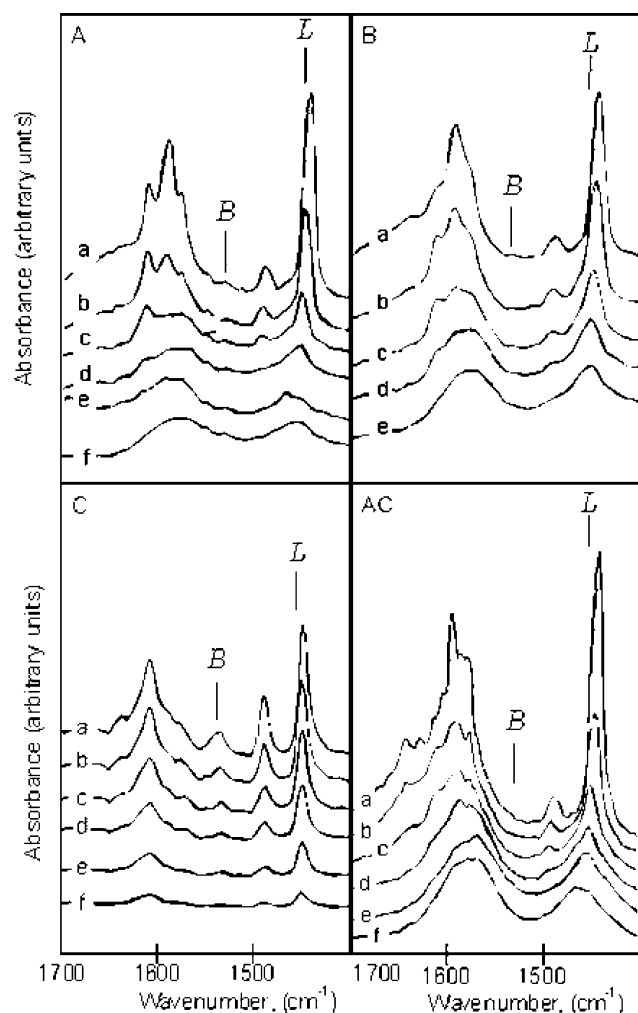


Fig. 7 Pyridine adsorption (FTIR) of sol-gel aluminas calcined at 500 °C

The pyridine thermodesorption spectra of calcined samples at 500 °C are shown in Fig. 7. The band at 1545 cm^{-1} is assigned to Brönsted sites and the band at 1450 cm^{-1} corresponds to pyridine coordinated to Lewis acid sites, meanwhile the band at higher energy 1490 cm^{-1} is associated to the presence of Brönsted and Lewis acid sites, due to the vibration of the aromatic pyridinic ring [16]. The presence of the band corresponding to Brönsted acid sites in alumina is due to the existence of Al-OH groups on the alumina surface [17]. The pyridine desorption in the samples was made at: a). 50 °C, b). 100 °C, c). 200 °C, d). 300 °C, e). 400 °C, and f). 500 °C. The sample prepared from aluminum ethoxide shows Brönsted acid sites (50 to 150 °C) while the other samples mainly present Lewis sites. The Brönsted and Lewis bands gradually disappear by increasing the temperature of desorption. However, strong Lewis acid sites can be observed in all

Table 3 Catalytic activity for the dehydration of 2-propanol of sol-gel aluminas

Sample	10^8 rate (mol/g s)	Propene selectivity (% mol)
A	105.8	81
B	82.8	80
C	50.3	80
AC	136.2	86

the samples since the band at 1450 cm^{-1} does not disappear even when the samples were heated at 500 °C under vacuum.

Table 3 shows the results for the catalytic activity in the dehydration of 2-propanol. It is observed that alumina prepared from the mixture of aluminum *sec*-butoxide and aluminum ethoxide showed the highest activity. During the hydrolysis of mixed alkoxides, a continuous exchange between the alkoxy groups has been reported [18]. In this sample, high structural heterogeneity can be developed, forming strong acid sites (Fig. 7). On the other hand, in the alumina prepared from aluminum ethoxide (sample C) small structural heterogeneity can be expected (close-packed structure) and hence weak acidity is developed. The lowest intensity peaks correspond to this sample in the pyridine-FTIR spectra. For the other samples (A and B) the acidity reached medium values. All the catalysts showed comparable selectivity to propene (80–86% mol). On the other hand, the formation of acetone was also of the same order (14–20% mol), showing that for aluminas prepared from aluminium alkoxide precursors acid-basic sites pair can be developed [19].

4 Conclusions

In the preparation of alumina by the sol-gel method, an important effect of the aluminum alkoxide precursors on the specific surface area, mean pore size diameter and pore size distribution is observed. A narrow pore distribution is obtained using aluminum ethoxide as precursor; meanwhile a broad pore size distribution is obtained with aluminum *sec*-butoxide and aluminum isopropoxide. Alumina prepared from *sec*-butoxide or isopropoxide produces aggregates in form of plates, forming slit-shaped pores. In alumina prepared from aluminum ethoxide the porous material consists of agglomerates of compact packing spheres. This is in agreement with the X-ray diffraction results, because the fresh sample prepared from the ethoxide does not present the formation of plates in its structure. Only the alumina prepared from aluminum ethoxide shows a large IR band corresponding to Brönsted acid sites (the

presence of this band is unusual in aluminas). The high activity in the dehydration of 2-propanol showed by the samples can be attributed to the structural heterogeneity developed during the preparation.

References

1. J. Livage, *Catal. Today*. **41**, 3 (1998)
2. J. Sanchez-Valente, X. Bokhimi, J.A. Toledo, *Appl. Catal. A: Gen.* **264**, 175 (2004)
3. B.E. Yoldas, *J. Mater. Sci.* **10**, 1856 (1975)
4. D.L. Trimm, A. Stanislaus, *Appl. Catal.* **21**, 215 (1986)
5. B.E. Yoldas, *J. Mater. Sci.* **10**, 1856 (1975)
6. B.E. Yoldas, *Am. Ceram. Soc. Bull.* **54**(3), 289 (1975)
7. T. Lopez, A. Romero, A. Chavela, L. Razo, R. Gomez, *React. Kinet. Catal. Lett.* **43**, 307 (1991)
8. K.S.W. Sing, et al. *Pure Appl. Chem.* **57**, 603 (1985)
9. F. Dumeignil, K. Sato, M. Imamura, N. Matsubayashi, E. Payen, H. Shimada, *Appl. Catal. A: Gen.* **241**, 319 (2003)
10. P. Raybaud, M. Digne, R. Iftimie, W. Wellens, P. Euzen, H. Toulhoat, *J. Catal.* **201**, 236 (2001)
11. R.I. Zakharchenya, *J. Sol-Gel Sci. Technol.* **6**, 179 (1996)
12. M. Fukuoka, *J. Sol-Gel Sci. Technol.* **1**, 47 (1993)
13. I. Jaymes, A. Douy, P. Florian, D. Massiot, J.P. Coutures, *J. Sol-Gel Sci Technol.* **2**, 367 (1994)
14. Corma A., J. Perez-Pariente, *Appl. Catal.* **63**, 145 (1990)
15. Wachs I.E., *Characterization of Catalytic Materials; II Series: Materials Catalytic Materials*. (Butterworth-Heinemann, Stone Ham, 1992)
16. H.H. Kung, in: *Studies in Surface Science and Catalysis, vol. 45*, ed. by B. Delmon, J.T. Yates (Elsevier, Amsterdam, 1989), p. 80
17. J. Sánchez-Valente, X. Bokhimi, F. Hernández, *Langmuir*. **19**, 3583 (2003)
18. C.J. Brinker, G.W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. (Academic Press, San Diego, CA 1990)
19. A. Gervasini, J. Fenyvesi, A. Auroux, *Catal. Lett.* **43**, 219 (1997)