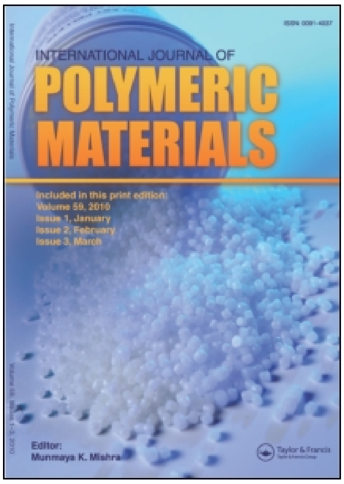

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Mendoza-Serna, R. , Loyo-Arnaud, E. , Roquero-García, C. E. , Rosas-Cedillo, R. and Moreno-Rodríguez, J. A.(2002) 'MICROPOROUS SOLIDS FROM SiO_2-Al_2O_3', International Journal of Polymeric Materials, 51: 6, 547 — 556

To link to this Article: DOI: 10.1080/00914030209696300
URL: http://dx.doi.org/10.1080/00914030209696300

International Journal of Polymeric Materials, 51:547–556, 2002
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0091-4037/02 \$12.00 + .00
DOI: 10.1080/00914030290046129

MICROPOROUS SOLIDS FROM SiO_2—Al_2O_3

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Polymeric Si—Al sols were prepared from $Al(OBu^s)_3$ and $Si(OEt)_4$ (TEOS). Acetylacetone and isoeugenol were employed separately to chelate the Al precursor in order to slow down the chemical reactivity, avoiding precipitation. The characterization techniques were Fourier Transform Infrared Spectroscopy (FTIR), nitrogen sorption measurements, Thermal Gravimetric (TGA) and Differential Thermal Analyses (DTA). The Si—O—Al bond vibration was detected by FTIR in the 1056–1074 cm^{-1} region. From the N_2 adsorption, isotherms the surface area results obtained range between 15.8 to 408.4 m^2/g. Corresponding average pore diameter are 3.397 to 1.417 nm. It is found that the porous texture of the materials mainly depends to the chelating agent in the sols. A strong influence of the molecular structure of the chelating agents in the sols was observed in the oxides by TGA and DTA studies.

Keywords: SiO_2—Al_2O_3, sol-gel, modifying agents, porous texture

INTRODUCTION

One of the main technological interests of the sol-gel process is related to the preparation of amorphous solids at low temperature. Amorphous silica-alumina catalysts are among the most widely used solid acid catalyst in the oil and chemical industries and are largely applied for isomerization of olefins, paraffins, and alkyl aromatics, alkylation of aromatics with alcohols and olefins, and olefins oligomerization and catalytic cracking [1]. In the

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Received 27 December 2000; in final form 31 December 2000.

R.M.S., E.L.A. and C.E.R.G. acknowledge U.N.A.M., DGAPA (Grant. PAPIIT no. IN 111198) for the financial support provided.

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inorganic membrane field, microporous materials are attracting more and more attention because of interesting, molecular sieve-like, gas separation properties [2]. The purpose of the present study is the spectroscopy study of the SiO_2—Al_2O_3 (molar ratio Si/Al = 91/9) system. Homogeneous and stable Si—Al polymers were synthesized, where molecular modification of $Al(OBu^s)_3$ was done using acetilacetone (2,4 pentanedione, acacH), and isoeugenol (2-methoxy-4-propenylphenol, isoH) separately as chelating agents. The Si precursor was $Si(OEt)_4$ (TEOS). The chemical reactivity of Al was controlled in this way and Al_2O_3 precipitation was avoided. AcacH has often been reported in the sol-gel literature as a stabilizing agent for $Al(OBu^s)_3$ [3, 4]. The polymeric route has been previously used for the preparation of SiO_2—ZrO_2 [5] and SiO_2—TiO_2 [6, 7].

EXPERIMENTAL

The chelating agents (c. a.) were used to stabilize Al: acacH and isoH, in both cases the molar ratio (c. a.)/Al was 3.0.

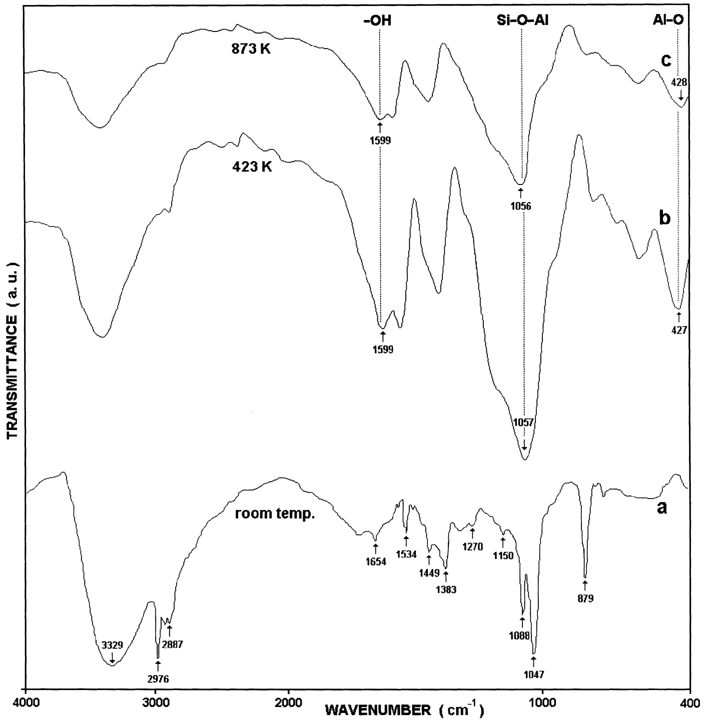

FIGURE 1 FTIR spectra of Si—Al(acac): (a) fresh sol, (b) xerogel dried at 423 K, and (c) solid calcined at 873 K.

Preparation of the Si—Al Sols

6.271×10^{-3} mol of $Al(OBu^s)_3$ (Aldrich) were dissolved in 0.206 mol of EtOH (Merck), 18.813×10^{-3} mol of chelating agent were dissolved separately in 0.171 mol of EtOH. The chelating agent sol was added to the Al sol. The sol was stirred during 15 min. An A2 sol [8, 9] was added dropwise to the chelating Al sol (addition time: five hours).

CHARACTERIZATION TECHNIQUES

The FTIR spectra of the sols and xerogels were obtained using a spectrophotometer Perkin Elmer 1600 in the 4000–400 cm^{-1} region using KBr plates. The N_2 adsorption isotherms of the xerogels were measured at 77 K in an Quantachrome Autosorb-1 after outgassing at 423 K for 12 h. Thermal analysis (DTA and TGA) were performed in a Stanton Redcroft STA780 instrument in air at a heating rate of 10°C/min in the 303–1273 K range.

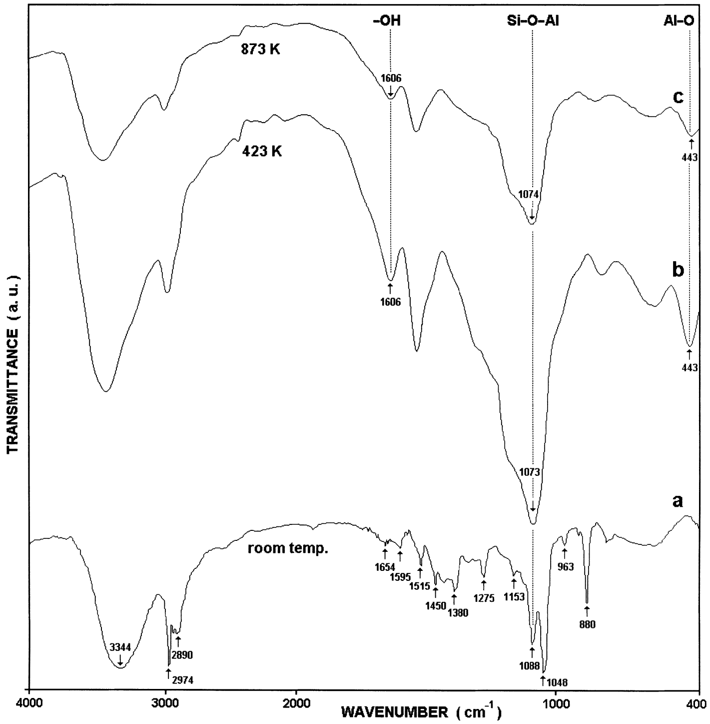

FIGURE 2 FTIR spectra of Si—Al(iso): (a) fresh sol, (b) xerogel dried at 423 K, and (c) solid calcined at 873 K.

RESULTS AND DISCUSSION

FTIR

The FTIR spectra obtained for the Si—Al(acac) fresh sol and xerogels dried 24 h. in air at 423 K and solids calcined at 873 K appear in Figure 1, the FTIR spectra for the Si—Al(iso) samples appear in Figure 2, the corresponding fresh sols assignment appear in Table 1. The band observed at 427 – 443 cm^{-1} in the spectra of xerogels and solids calcined is assigned to Al—O groups [20]. The most important characteristic in all spectra from sols to xerogels and solids calcined was the permanence of the Si—O—Al bands. These appeared in the 1074 – 1056 cm^{-1} region.

Textural Characteristics

With the BET method, the nitrogen adsorption-desorption isotherms at 77 K allows the measurement of the specific surface area. The isotherms for the samples Si—Al(acac) and Si—Ti(iso) appear in Figures 3 and 4 respectively. A type 1 isotherm [21] was found for the all samples. In the samples Si—Al(acac) the isotherms present a large portion of hysteresis loop covers all P/Po range, suggesting the pore structure is broad (overlapping both the micropore and mesopore region) [21, 22]. The extend of non-closure of the hysteresis loop of the Si—Al(acac) samples is biggest at 423 K. The isotherms of the Figure 4 too present the case where micropores are present

TABLE 1 FTIR bands assignment in fresh Si—Al(acac) and Si—Al(iso) sols

	Wavenumber (cm^{-1})	
Assignment	*Si—Al(acac)*	*Si—Al(iso)*
O—H stretching	3329	3344
C—H stretching [10, 11]	2976	2974
	2887	2890
O—H bending in free H_2O [12]	1654	1654
C=C stretching [13]		1595
		1515
C=C and C=O stretching in acacH [4, 14]	1534	
Symetric and Assymetric C—H vibrations (TEOS, ethoxy groups) [15]	1449	1450
	1383	1380
	1270	1275
Asym. deformation vibration of AlO—H [16]	1150	1153
Si—O—Al [10, 17]	1088	1088
Si—O—Si [10]	1047	1048
Si—OH [18]		963
Si—OH and absorptions of EtOH [19]	879	880

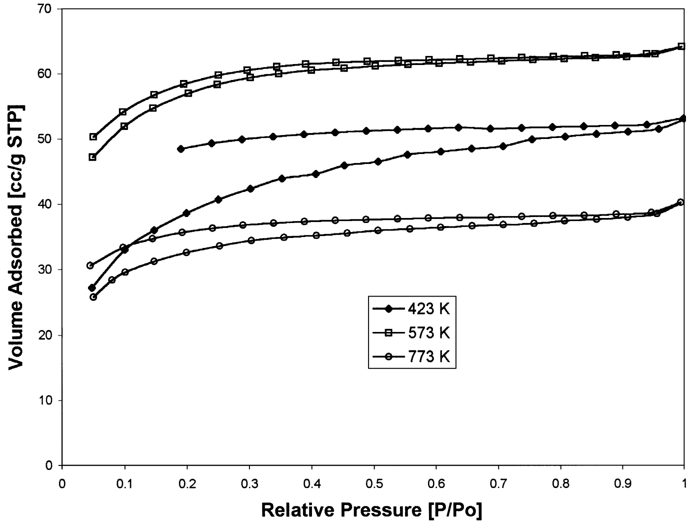

FIGURE 3 Nitrogen adsorption/desorption isotherms for Si—Al(acac).

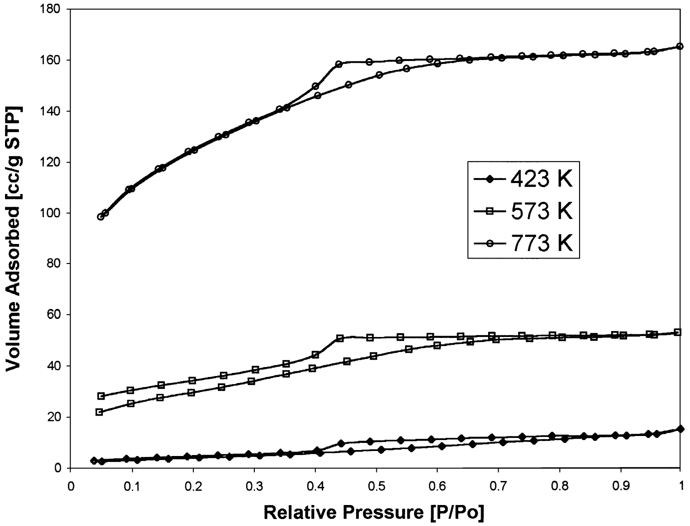

FIGURE 4 Nitrogen adsorption/desorption isotherms for Si—Al(iso).

along with mesopores [21, 23]. The pore diameters distribution curves of the Si—Al(acac) samples are shown in Figures 5 and 6. The Figures 7 and 8 shown the pore diameters distribution curves of the Si—Al(iso). The Horváth-Kawazoe model was used too because the two models together

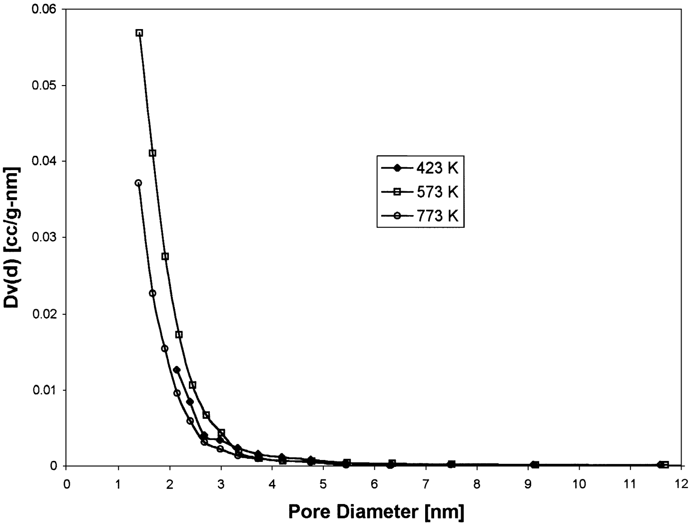

FIGURE 5 Pore size distribution of the Si—Al(acac) samples.

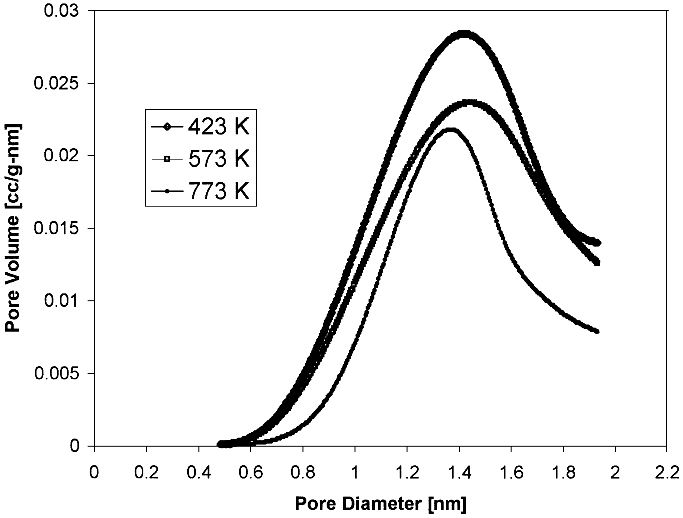

FIGURE 6 Pore size distribution of the Si—Al(acac) samples according to the Horváth-Kawazoe model.

cover the full range of the pore sizes [24]. In both systems the pore size diameter decreased on heating. The BET surface areas, pore volumes and the mean pore diameters of the samples are summarized in Table 2. The

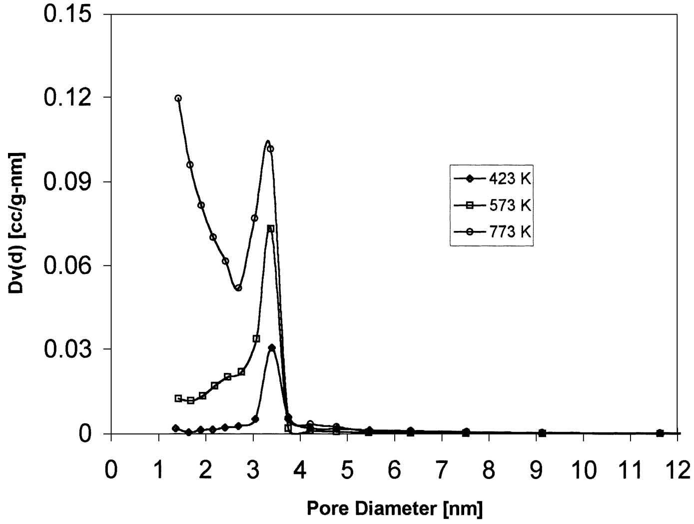

FIGURE 7 Pore size distribution of the Si—Al(iso) samples.

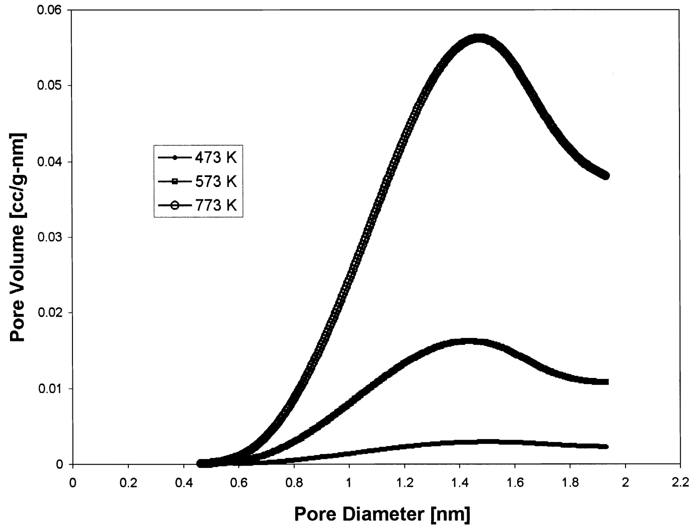

FIGURE 8 Pore size distribution of the Si—Al(iso) samples according to the Horváth-Kawazoe model.

textural measurements of the solids: surface area, size-distribution of pores and average pore diameter depend of temperature and the chelating agent used.

TABLE 2 Porosimetry data for the Si—Al samples

Sample	*Temperature* (*K*)	*BET surface area* (*m*^{2}/*g*)	*BJH pore volume* (*cm*^{3}/*g*)	*Average pore diameter* (*nm*)
Si—Al(acac)	423	129.3	0.0782	1.421
	573	175.1	0.0479	1.425
	773	105.4	0.0312	1.407
Si—Al(iso)	423	15.8	0.0259	3.397
	573	105.4	0.0643	3.386
	773	408.4	0.198	1.417

DTA and TGA

The DTA/TGA curves of Si—Al(acac) and Si—Al(iso) are given in Figures 9 and 10, respectively. In Si—Al(acac) two weight loss were observed. The first one was 13.2% and occurred in the range 303 – 493 K and it was associated to an endothermal peak at 388 K. These changes are due to the elimination of solvent and H_2O. The second one was 25.3% and occurs in the range 493 – 873 K and it was associated to an exothermal peak at 733 K and corresponds to the burning of organic residue. In Si—Al(iso) the first weight loss observed was 21% and occurred in the range 303 – 573 K and it was associated to an endothermal peak at 398 K. The second weight loss observed was 31% and occurred in the range 573 – 1273 K it was associated to three exothermal peaks at 773, 1013 and 1253 K. The peak at 1013 K could be due to the oxidation of the residual organics [25]. The exothermal

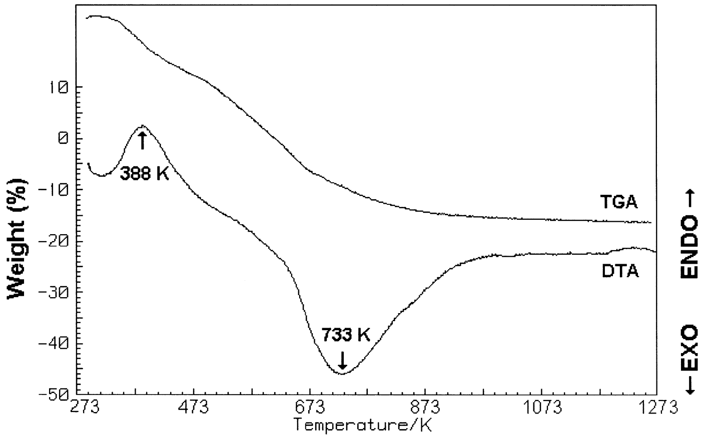

FIGURE 9 DTA/TGA curves of Si—Al(acac).

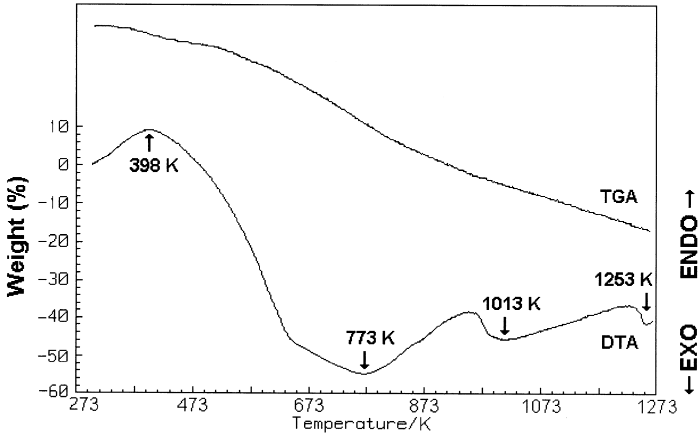

FIGURE 10 DTA/TGA curves of Si—Al(iso).

peak observed at 1253 K is closely related to a good mixing degree of the Al and Si species [26–28]. The differences in weight loss and temperature of the peaks between the two samples are due to the molecular weight and structure of the chelating agents.

CONCLUSIONS

Stable Si—Al sols were obtained using acacH and isoH as Al modifying agents. The FTIR vibration bands of the Si—O—Al bonds detected in the sols, xerogels and oxides calcined up to 873 K indicate that those are stable bonds and that Al were homogeneously incorporated to the Si network. The N_2 adsorption-desorption isotherms indicate that all the samples have micropores with mesopores. The exothermal peak at 1253 K indicates a better homogeneity in the degree of mixing of the Al and Si components in the Si—Al(iso) gels. The slow elimination of the organic residue in both samples can be attributed to a microporous structure of the solids.

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