Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 110, No. 2, April 1998, pp. 143–149.

Mesoporous alumina

NEERAJ and M ESWARAMOORTHY*
Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560012, India

MS received 30 March 1998

Abstract. Alumina with a fairly large surface area ($415\,m^2g^{-1}$) and narrow pore size distribution (pore diameter ~ 3 nm), containing octahedral and tetrahedral aluminum, prepared by long chain neutral amine as the surfactant, shows some evidence of textured structure. This material also contains disordered hexagonal structures, but use of partially hydrolyzed aluminum alkoxide with short chain amine templates, results in amorphous alumina with a surface area of $340\,m^2g^{-1}$. Use of a polyethylene oxide as the surfactant, did not give the mesoporous structure in the absence of the template.

Keywords. Mesoporous alumina; ^{27}Al MASNMR; textural mesoporosity; BJH method; transmission electron microscopic images.

1. Introduction

High surface area alumina is of vital interest in catalysis. Although there are several reports in the literature on the synthesis of porous alumina, most of the preparations seem to possess purely textural porosity or are amorphous [1–3]. There have been some recent efforts to prepare mesoporous alumina, but they have not been successful in obtaining ordered structures. Yada *et al* [4] prepared alumina by the homogeneous precipitation method using urea, and obtained a product with a somewhat disordered structure ($d_{100} = 3{\cdot}4$ nm). Vaudry *et al* [5] have prepared alumina mesophases starting with a mixture of aluminum sec–butoxide and aliphatic carboxylic acids. They obtained high surface area alumina with a mesoporous structure which is not well defined. Bagshaw *et al* [6] have examined alumina prepared by the hydrolysis of aluminum sec-butoxide in the presence of polyethylene oxide surfactants, and found the presence of worm-like structures with no long-range order. It therefore seems that alumina with a reasonably ordered hexagonal mesoporous structure has not been prepared hitherto.

In this communication, we report the synthesis of mesoporous alumina by the neutral amine route [7]. A specific advantage of the method is that the long chain amine template, which is weakly hydrogen bonded to the metal alkoxide, is readily removed. We have also employed polyoxyethylene sorbitanmonooleate (Tween 80) as the template to prepare mesoporous alumina. We have attempted to prepare mesoporous alumina by making use of short chain amines and partially hydrolyzed aluminum iso-propoxide [8].

*For correspondence

2. Experimental

In a typical synthesis, aluminum sec-butoxide (0·01 mol) was added to an ethanolic solution (10 ml) of dodecylamine or hexadecylamine (0·0082 mol). Water (5 ml) was added to this mixture in a dropwise manner, under stirring. The gel thus obtained was aged at 323 K for 22 h, filtered and washed with acetone. The X-ray diffraction (XRD) patterns (CuK_α radiation) of the dried products showed reflections at *d*-values of 5·8 nm and 6·3 nm respectively with dodecylamine and hexadecylamine templates as shown in figures 1(a) and (b). FT-IR spectra of as-prepared samples showed the expected bands due to CH_2, NH_2 and other group vibrations. Thermogravimetric analysis (TGA) showed loss of the elements of water at 423 K and complete loss of the template around 823 K, just as in the hexagonal mesoporous structure prepared by electrostatic interactions [9,10].

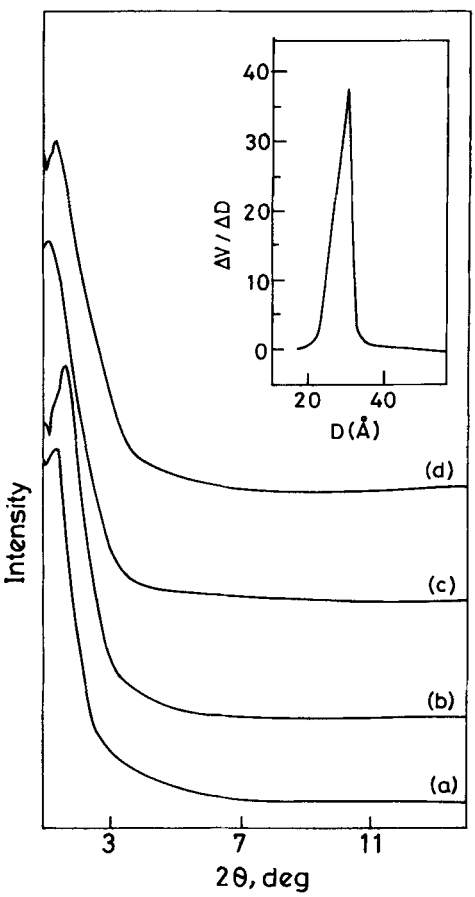

Figure 1. X-ray diffraction patterns of alumina prepared with (**a**) dodecylamine and (**b**) hexadecylamine as templates. The diffraction patterns of the corresponding calcined samples are shown in (**c**) and (**d**) respectively. The inset shows the pore size distribution in a calcined sample (prepared with dodecylamine).

The procedure for synthesis with polyoxyethylene sorbitanmonooleate (Tween 80) as surfactant was similar to that employed for long chain amines as template. Here aluminum sec-butoxide (10 mmol) was added to an ethanolic solution (10 ml) of the surfactant (0·3 ml). We also tried to prepare mesoporous alumina by using partially hydrolyzed aluminum iso-propoxide. In this experiment, hexylamine/octylamine (3·8 mmol) was taken in isopropanol (10 ml) and stirred for 10 min. To this, aluminum iso-propoxide (5 mmol) partially hydrolyzed with water (83 mmol) was added. The mixture was stirred for 30 min and the resulting gel was aged at 298 K for 20h, filtered, washed with water and dried at 363 K.

3. Results and discussion

Based on the TGA data, the compositions of the hexagonal amine adduct of alumina work out to be $Al_2O_3 \cdot 2H_2O$.amine and $Al_2O_3 \cdot H_2O$.amine with dodecylamine and hexadecylamine respectively. On heating the amine adducts at 773 K for 6h, it was possible to remove the amines entirely, the resulting products showing reasonably sharp XRD reflections at *d*–values of 9·4 nm and 8·0 nm for dodecylamine and hexadecylamine respectively, as can be seen in figure 1(c) and (d). FT-IR spectra of the calcined samples showed the absence of the characteristic bands of the amine and also a decrease in the band due to OH/H_2O in the 3000–3600 cm^{-1} region. It is not entirely clear why the d_{100} spacing in XRD pattern increases from $\sim$ 6 nm to 8·0–9·0 nm on calcination. Such large *d*-spacings are known in disordered silicas [7,9,11,12], but we believe that the structure gets reorganized and textured after calcination. The X-ray diffraction profiles in figure 1 and the electron microscopic images suggest the presence of some disordered hexagonal structures.

Transmission electron microscopy (TEM) images of the as-prepared mesoporous alumina samples as well as those of the corresponding calcined samples reveal interesting structural features. The as-prepared samples possess a disordered lamellar structure as shown in the TEM image in figure 2(a). This structure probably corresponds to the so-called worm-like features reported by Bagshaw and Pinnavaia [12]. The lamellar or worm-like structure is however more distinct in the images obtained by us. The calcined samples show the presence of hexagonal mesopores though disordered, as can be seen from the TEM image in figure 2(b). The average pore diameter from the image is $\sim$ 3 nm. The images in figures 2(a) and (b) represent the lamellar-to-hexagonal transformation of mesoporous alumina brought about thermally, on the removal of the amine template. The lamellar-like structure in figure 2(a) corresponds to a layer separation of 2·8 nm which is exactly what we would expect for a lamellar phase prepared with the dodecylamine with a chain length of 1·4 nm. The *d*–spacing of 5·8 nm of the as-prepared sample is however, roughly twice the interlamellar spacing. The d_{100} value of $\sim$ 9·0 nm of the calcined sample roughly corresponds to three times the interlamellar spacing.

^{27}Al MASNMR spectra of the alumina samples subjected to different treatments are shown in figure 3. The as-prepared sample shows a signal close to 0 ppm due to octahedral aluminum [13]. On dehydration at 423 K, the spectrum does not show any significant change. However, on calcination, a new feature emerges around 69 ppm due to tetrahedrally coordinated aluminum. The ratio of the octahedral to the tetrahedral Al is approximately 75:25. The proportion of the penta-coordinated aluminum, if any, seems to be negligible, since we see no measurable intensity in the 35 ppm region [5].

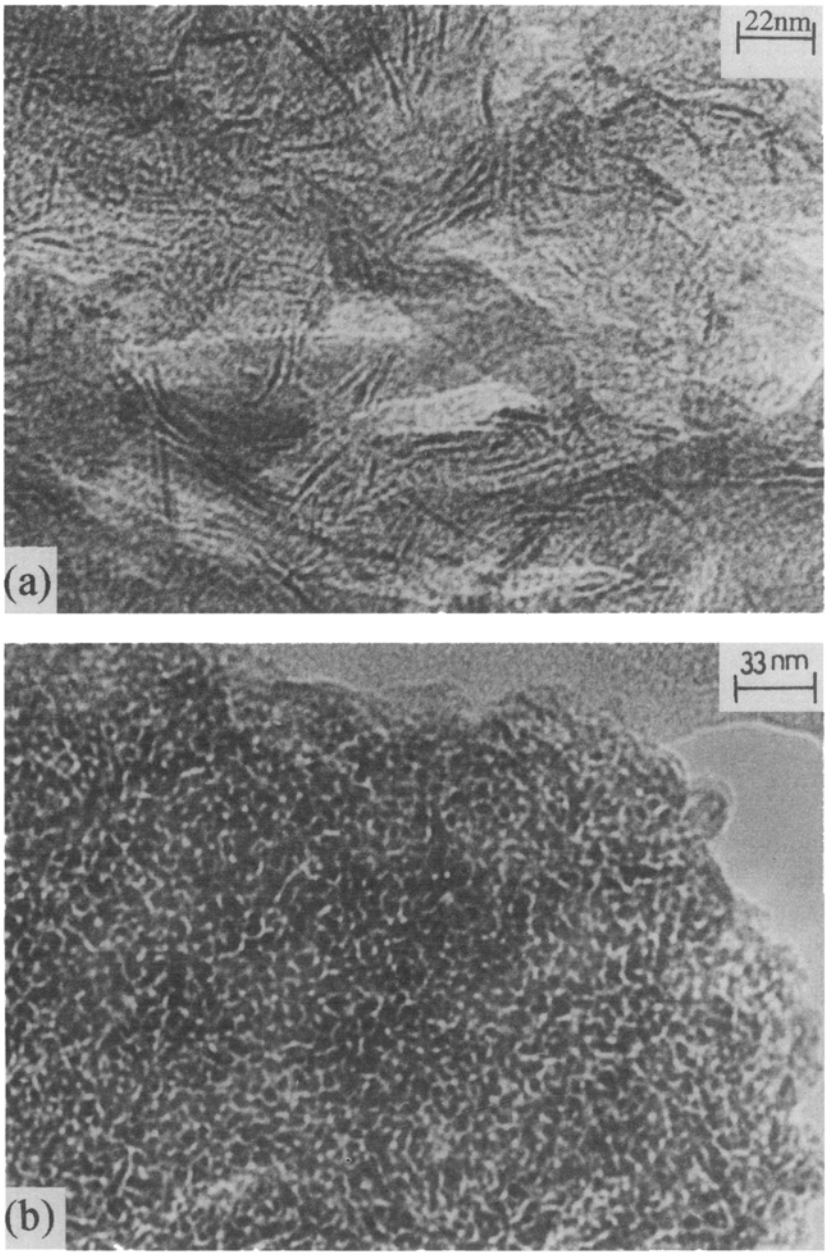

Figure 2. Transmission electron microscopic images (**a**) of the as-prepared alumina (with dodecylamine) and (**b**) of the calcined sample.

We have measured the N_2 adsorption isotherms of the mesoporous alumina sample prepared. Figure 4 shows the N_2 adsorption-desorption isotherm for a hexagonal alumina adduct obtained with dodecylamine template and calcined at 773 K. It shows small steps in adsorption isotherm between $p/p_0 \sim 0{\cdot}4$–$0{\cdot}9$ characteristic of disordered hexagonal pores and a broad hysterisis in the desorption isotherm over the same

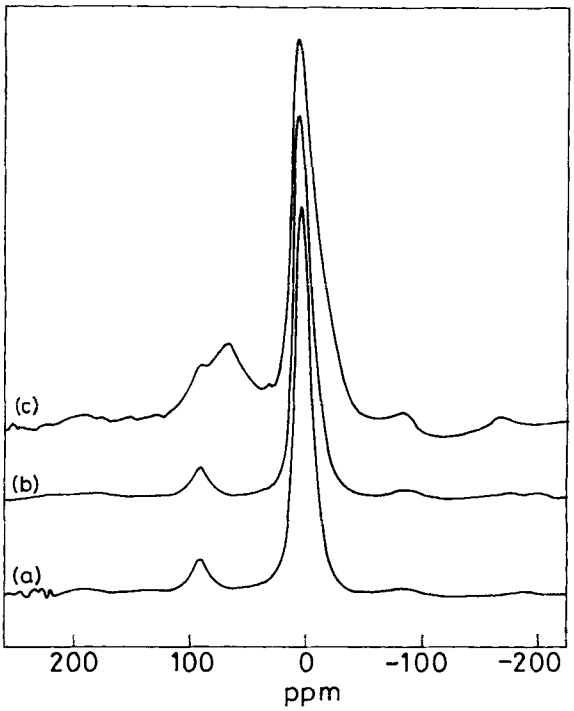

Figure 3. ^{27}Al MASNMR spectra of the alumina samples (**a**) prepared with dodecylamine, (**b**) of the dehydrated sample and (**c**) of the calcined sample.

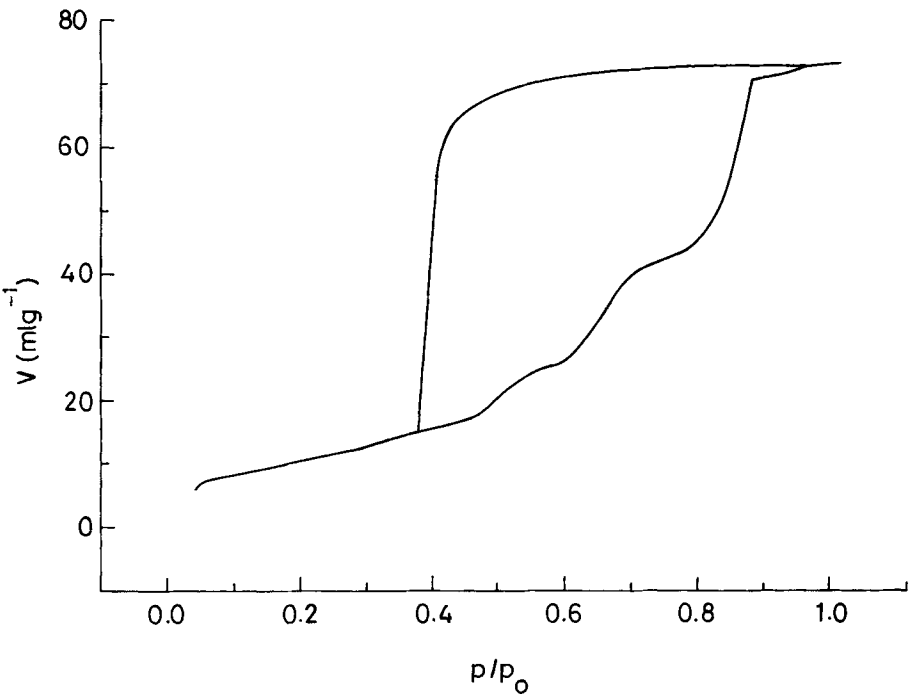

Figure 4. N_2 adsorption-desorption isotherm of the calcined alumina (with dodecylamine).

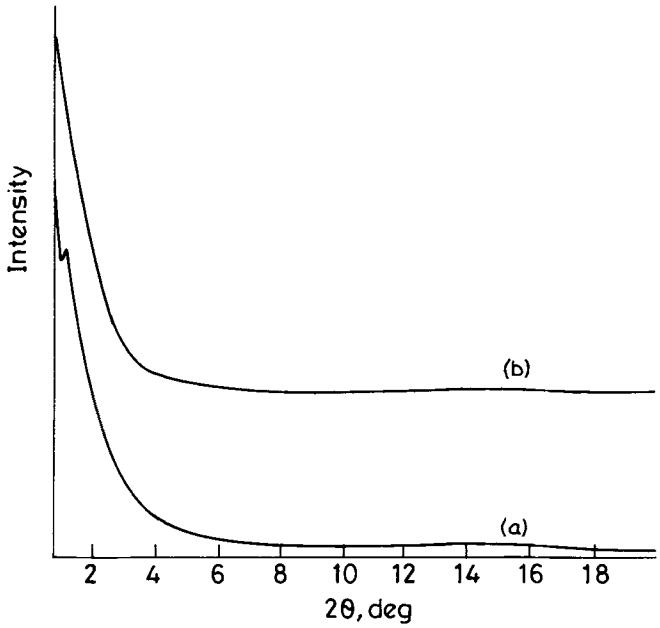

Figure 5. X-ray diffraction patterns of alumina prepared with (**a**) Tween 80 (**b**) hexylamine.

relative partial pressures. The hysterisis loop till $p/p_0 \sim 0{\cdot}9$ suggests textural mesoporosity [12]. The BET surface areas for the samples obtained with dodecylamine and hexadecylamine were $405\,m^2g^{-1}$ and $377\,m^2g^{-1}$ respectively, the surface areas not high enough as expected of hexagonal mesoporous phase. By employing the Barrett-Joyner-Halender (BJH) method [14] of analysis of the adsorption and desorption isotherms, we have obtained the pore size distribution in a calcined sample of alumina prepared with dodecylamine as the template. The distribution is narrow and is centred at 3 nm, consistent with the average pore size revealed in some of the TEM images.

With Tween 80, we obtained the hexagonal alumina adduct (figure 5(a)), but the mesostructure collapsed on calcination at 773 K for 6 h. The BET surface area of the calcined sample was $300\,m^2\,g^{-1}$. Our attempts to synthesize mesoporous alumina using partially hydrolysed aluminum iso-propoxide resulted in amorphous alumina (see figure 5(b) for the XRD pattern). However, the BET surface area of the samples calcined at 773 K for 10h was $\sim 340\,m^2g^{-1}$ which is comparable to that obtained earlier with the amine.

Acknowledgement

We are grateful to Prof C N R Rao for his guidance and invaluable suggestions during the course of this investigation.

References

1. Adkins H and Watkins S H 1951 *J. Am. Chem. Soc.* **73** 2184
2. Basmadjian D, Fulford G, Parsons B I and Montgomery D S 1962 *J. Catal.* **1** 547

3. Chen C-M, Chen S–Y and Peng S–Y 1995 *Stud. Surf. Sci. Catal.* **91** 427
4. Yada M, Machida M and Kijima T 1996 *Chem. Commun.* 769
5. Vaudry F, Khodabandeh S and Davis M E 1996 *Chem. Mater.* **8** 1451
6. Bagshaw S A and Pinnavaia T J 1996 *Angew. Chem. Int. Ed. Engl.* **35** 1102
7. Tanev P T and Pinnavaia T J 1995 *Science* **267** 865
8. Sun T and Ying J Y 1997 *Nature (London)* **389** 704
9. Huo Q, Margolese D I, Ciesla U, Demuth D G, Feng P, Gier T E, Sieger P, Firouzi A, Chmelka B F, Schuth F and Stucky G 1994 *Chem. Mater.* **6** 1176
10. Huo Q, Margolese D I, Ciesla U, Feng P, Gier T E, Sieger P, Leon R, Petroff P M, Schuth F and Stucky G 1994 *Nature (London)* **368** 317
11. Chen C Y, Li H Y and Davis M E 1993 *Microporous Mater.* **2** 17
12. Bagshaw S A, Pronzet E and Pinnavaia T J 1995 *Science* **269** 1242
13. Akitt J W 1989 *Prog. Nucl. Magn. Reson. Spectrosc.* **21** 127
14. Barrett E P, Joyner L G and Halender P P 1951 *J. Am. Chem. Soc.* **73** 373