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Aluminium oxide grafted on silica gel surface: Study of the thermal stability, structure and surface acidity

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The synthesis of aluminium oxide grafted on silica gel surface was carried out by the reaction of a suitable aluminium precursor with the surface hydroxyl groups, ≡SiOH, of the oxide support in non-aqueous solvent. The advantage of this preparation method, compared to the conventional ones (impregnation or precipitation and calcination), is that the oxide is highly dispersed on the surface (monolayer or submonolayer). The resulting material, SiO_2/Al_2O_3, was heat treated at temperature range of 423 to 1573 K. The Al/Si atomic ratios, determined by X-ray photoelectron spectroscopy (XPS), showed that aluminium is less mobile up to heat treatment of 1173 K and above this temperature part of it diffuses to the interior of the matrix. ^{27}Al solid state nuclear magnetic resonance spectroscopy (NMR) showed two different environments, tetrahedral and octahedral for sample calcined up to 1023 K and above this temperature, aluminium in a trigonal bipyramidal environment was also detected. Pyridine adsorbed on a Lewis acid sites were observed for samples calcined up to 1023 K, and above this temperature they were not detected. *© 2000 Kluwer Academic Publishers*

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1. Introduction

The study of highly dispersed Al_2O_3 on SiO_2 surface is of interest taking into account its numerous uses, especially in catalytic reactions [1, 2]. Its properties can be quite different of that in bulk phase [3]. The quantity of the exposed active acid centres in metal oxide monolayer films is considerably higher than for bulk phase oxide, and the Lewis acid sites are very stable under heat treatments because the oxides are attached to the surface by Si–O–M bonding and are less mobiles, avoiding the collapse of the particles and deactivation of the Lewis acid sites [4].

The structures of numerous alumina are known [5–8], but those of highly dispersed oxide structures on a porous substrate solid matrix are less known. In a recent work, a series of high area silica gel substrate treated with well characterised aluminium solutions was prepared and the structure of the obtained SiO_2/Al_2O_3 studied by Magic Angle Spinning (MAS) ^{27}Al NMR spectroscopy [9].

In this work, the preparation of SiO_2/Al_2O_3 was carried out by reacting SiO_2 with $Al(OR)_3$ [$R = (CH_3)_2CH–$] in non-aqueous solvent. The reaction of alkoxide with silanol groups, ≡SiOH, occurred readily, yielding Al–O–Si bond formation. In this case, only monolayer or sub-monolayer can be formed on the substrate surface. The structure, thermal stability and the acidity of the grafted species are discussed.

2. Experimental

Aluminium oxide was grafted on silica gel surface by immersing 70 g of silica gel (Aldrich, $S_{BET} = 460$ $m^2\,g^{-1}$, average diameter pore of 6 nm and particle sizes between 0.2 and 0.05 mm), heated at 423 K under vacuum (10^{-3} torr) in 250 ml of 0.14 M toluene solution of aluminium isopropoxide (Aldrich). The suspension was refluxed under nitrogen atmosphere for 24 h. The mixture was filtered under nitrogen atmosphere, washed with dry ethanol and heated under vacuum in order to

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eliminate all solvent. Furthermore, the solid was immersed in bidistilled water to promote the hydrolysis of the unreacted Al–O–R bond, filtered, washed with water, and dried at 393 K under vacuum for 8 h. The following chemical equations describe the preparation reactions:

$$n{\equiv}\mathrm{SiOH} + [(\mathrm{CH_3})_2\mathrm{CHO}]_3\mathrm{Al} \rightarrow$$
$$({\equiv}\mathrm{SiO})_n\mathrm{Al}[\mathrm{OCH}(\mathrm{CH_3})_2]_{3-n} + n(\mathrm{CH_3})_2\mathrm{CHOH}$$
$$({\equiv}\mathrm{SiO})_n\mathrm{Al}[\mathrm{OCH}(\mathrm{CH_3})_2]_{3-n} + (3-n)\mathrm{H_2O} \rightarrow$$
$$({\equiv}\mathrm{SiO})_n\mathrm{Al}(\mathrm{OH})_{3-n} + (3-n)(\mathrm{CH_3})_2\mathrm{CHOH}$$

where $\equiv$SiOH stands for silanol group on silica gel surface.

The quantity of Al incorporated in $(\equiv\mathrm{SiO})_n\mathrm{Al}(\mathrm{OH})_{3-n}$, hereafter designated as $\mathrm{SiO_2/Al_2O_3}$, was determined by using the X-ray fluorescence spectroscopy. The quantity of aluminium grafted on the silica gel surface was 1.92 wt%, corresponding to 0.73 mmol $\mathrm{g^{-1}}$.

Fine-grained samples of $\mathrm{SiO_2/Al_2O_3}$ ground as fine powder, were previously heat treated during 8 h at the following temperatures: 423, 573, 873, 1023, 1173, 1323, 1473 and 1573 K. The specific surface areas of the samples were obtained by the BET multipoint method on an ASAP 2010 equipment.

The X-ray diffraction (XRD) patterns of the heat-treated $\mathrm{SiO_2/Al_2O_3}$ and $\mathrm{SiO_2}$ powders were obtained on a Shimadzu XD3A X-ray diffractometer using a Cu $\mathrm{K_\alpha}$ radiation source.

The XPS analyses were performed in ultra-high vacuum (low 10^{-9} Torr range) using a KRATOS XSAM HS spectrometer. It was used Mg $\mathrm{K_\alpha}$ ($h\nu = 1253.6$ eV) as X-ray source, with power given by emission of 15 mA and voltage of 15 kV. The high resolution spectra were obtained with an analyser pass energy of 20 eV. The samples were flooded with low energy electrons from a flood gun to avoid charging effects. The binding energies were referred to adventitious carbon 1s line set at 284.8 eV. A least-square routine was used for peak-fitting.

The MAS ^{27}Al NMR spectra were obtained using a Bruker AC 300/P spectrometer. It was used an interval between pulses of 1 s and acquisition time of 49 ms. The chemical shift of an external standard acqueous 1.0 mol $\mathrm{l^{-1}}$ $\mathrm{Al(NO_3)_3}$ in 0.1 mol $\mathrm{l^{-1}}$ $\mathrm{HN_3}$ solution was used for calibration.

The infrared spectra were obtained on a Bomen MB series spectrometer using a Jasco DR 81 diffuse reflectance accessory. About 0.5 g of $\mathrm{SiO_2/Al_2O_3}$ was previously degassed at 10^{-3} torr and furthermore submitted to pyridine vapour for few minutes and the excess eliminated under vacuum for 4 h at 473 K.

3. Results and Discussion

Fig. 1 shows the variation of the specific surface areas of unheated sample (dried at 298 K under vacuum) and the samples heat treated up to 1573 K. The area of the native silica is 460 $\mathrm{m^2\ g^{-1}}$ and that of unheated $\mathrm{SiO_2/Al_2O_3}$ is 416 $\mathrm{m^2\ g^{-1}}$. The small area decrease of the surface is presumably due to the finest pores blocking of the silica matrix by the reagent upon chemical modification [10]. The specific surface areas also decreased as the samples were heat-treated at higher temperatures, and at 1173 K the materials became non-porous. Since this behaviour may be related with $\mathrm{Al_2O_3}$ mobility on the surface with diffusion into the interior of the matrix and simultaneous sintering of the silica matrix under thermal treatment, the XRD patterns of $\mathrm{SiO_2/Al_2O_3}$ heat treated at various temperatures were obtained (Fig. 2). It is observed that up to 1023 K the material remains amorphous, between 1323 and 1473 K (Figs 2d and e) some diffraction lines appear, and at 1573 K (Fig. 2f) it becomes crystalline. The diffraction peaks match

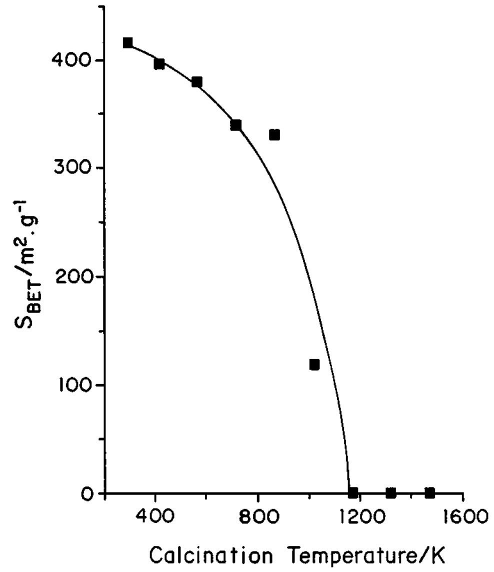

Figure 1 Variation of the specific surface area of $\mathrm{SiO_2/Al_2O_3}$ calcined at various temperatures.

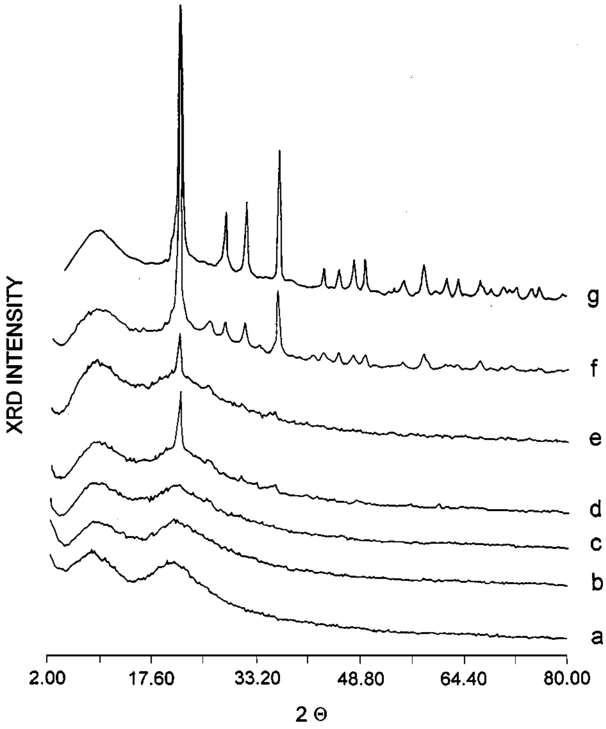

Figure 2 X-ray diffraction line intensities of $\mathrm{SiO_2/Al_2O_3}$ calcined at: a) dried at room temperature under vacuum, b) 1023 K, c) 1173 K, d) 1323 K, e) 1473 K, f) 1573 K, g) $\mathrm{SiO_2}$ calcined at 1573 K.

those of crystalline SiO_2 calcined at same temperature in similar condition (Fig. 2g), which correspond to α-cristobalite [11]. The dispersed Al_2O_3 remains amorphous in the heat treated matrix at various temperatures.

Table I summarises the XPS results. Two oxygen 1s peaks, resolved by curve fitting, can be distinguished: a) one between 531.1 and 532.3 eV, designated as O^I, and b) other between 532.6 and 534.2 eV, designated as O^{II}. The number in parenthesis is the atomic percentage of each contribution to the O 1s peak. The O^{II} peak is not observed for sample calcined above temperature of 1023 K. The O 1s binding energy for SiO_2 gel is 532.7 eV, and for various aluminosilicate compounds it occurs between 530.2 and 532.4 eV [12–14]. The Al/Si atomic ratios decreased as the temperature of calcination increased, presumably due to the diffusion of aluminium atom to the interior of the matrix. On the basis of this observation, it is possible to assign the O 1s peak of SiO_2 to O^I, and the other to O^{II}, i.e. O1s peak for Al_2O_3 in SiO_2/Al_2O_3.

The binding energies reported in the literature [12–14] for Si 2p of SiO_2 (gel or crystalline) occur between 103.3 and 103,7 eV; for Al 2p of Al_2O_3, between 73.5 and 74.1 eV, and of Al_2SiO_5 specimens, between 74.6 and 74.8 eV. Comparing these values with those listed in Table I, there is a clear indication that the species present on the surface is the Al_2SiO_5 phase, tetra- or hexacoordinated aluminium (III) immobilised on the surface by Al–O–Si bond [15], and not a separated Al_2O_3 phase. The agglomerate separated phase of Al_2O_3 particles are presumably in the interior of the matrix, as suggested by the decrease of S_{BET} of the unheated SiO_2/Al_2O_3 sample, and are not probed by XPS.

Fig. 3 shows the MAS ^{27}Al NMR spectra of the SiO_2/Al_2O_3 samples. The observed spectra are broad because Al_2O_3 are amorphous in all heat treated samples. Two lines, one at 0 ppm and other at 55 ppm for sample dried at room temperature under vacuum, are observed. The first line is assigned to aluminium in an octahedral environment, Al_{oct}-$(SiO_4)_6$, and the second one to aluminium in a tetrahedral environment, Al_{tetr}-$(SiO_4)_{tetr}$ [9]. Heating the sample, the octahedral line shifts from 0 to 10 ppm at 723 K and it remains invariant up to 1573 K. The tetrahedral line does not shift under heat treatment but increasing the temperature above 1323 K it becomes broadened and splits into two peaks, with the new one at 35 ppm. In bulk Al_2O_3 calcined at 973 K this new band is assigned to aluminium in a pentacoordinated trigonal bipyramidal environment, Al_{tbp}-$(SiO_4)_5$ according to the study made by Fripiat *et al.* [16] on gibbsite and boehmite. However, the pentacoordinated species are not normally found for bulk Al_2O_3 phase treated at high temperatures, as for instance above 1073 K, as shown in Fig. 3. Therefore, the Al_{tbp}-$(SiO_4)_5$ phase detected for the SiO_2/Al_2O_3 samples calcined at high temperatures for long time is presumably related to this species which diffused into the SiO_2 pores and stabilised in this form.

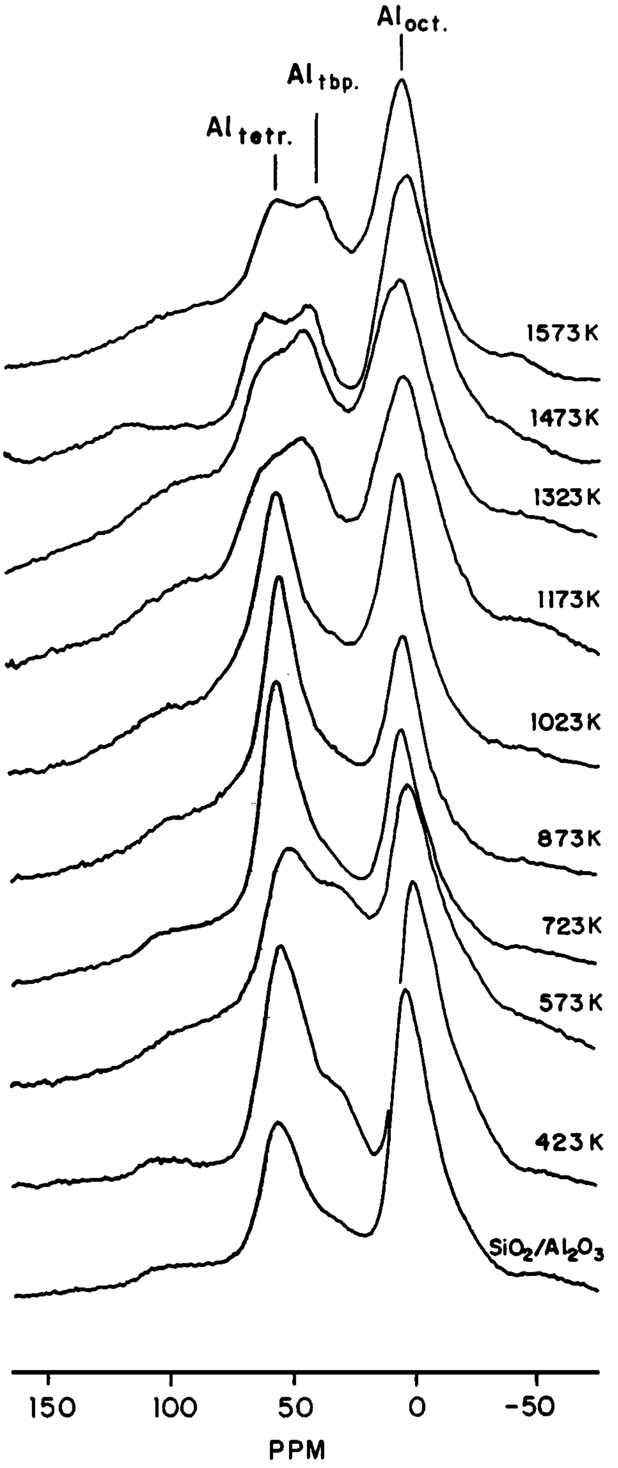

Figure 3 MAS ^{27}Al NMR of SiO_2/Al_2O_3 calcined at various temperatures. The first spectrum is of the sample dried under vacuum at room temperature.

The Lewis acid sites, as well as their stabilities, were studied by sorbing pyridine as a molecular probe on the surfaces of the pre-calcined samples. Fig. 4 shows the infrared spectra. For the sample dried under vacuum at room temperature and samples heat treated between 573 and 1023 K, the weak bands observed at ca.1600 cm^{-1} and ca.1450 cm^{-1} are assigned to the 8a and 19b vibrational modes, respectively, of pyridine coordinated to a Lewis acid site [17–19]. For samples calcined at 1173 K and above this temperature the Lewis acid sites are not observable. This is a confirmation that under heat treatment aluminium oxide diffuses to the interior of the matrix, which sinters at higher temperatures. The spectrum of py adsorbed on SiO_2 was recorded as a reference.

TABLE I XPS data for SiO_2/Al_2O_3 calcined at various temperatures

	Binding energy (eV)				Atomic ratios		
	O1s						
Temp. (K)	O^I	O^{II}	Si2p	Al2p	Al/Si	Al/O	Si/O
—	531.1 (32)	532.6 (68)	103.1	74.7	4.55	0.30	0.067
423	531.5 (51)	532.8 (49)	102.8	74.6	2.51	0.35	0.14
573	531.9 (86)	533.6 (14)	103.0	74.9	2.29	0.31	0.14
723	532.0 (86)	533.4 (14)	103.1	75.0	2.34	0.34	0.14
873	531.9 (87)	533.6 (13)	103.2	75.1	2.87	0.37	0.13
1023	532.3 (95)	534.2 (5)	103.3	75.2	2.73	0.36	0.13
1173	532.3		103.3	75.2	2.61	0.41	0.16
1323	532.3		103.2	75.1	1.22	0.27	0.22
1473	532.3		103.2	75.0	1.53	0.30	0.19

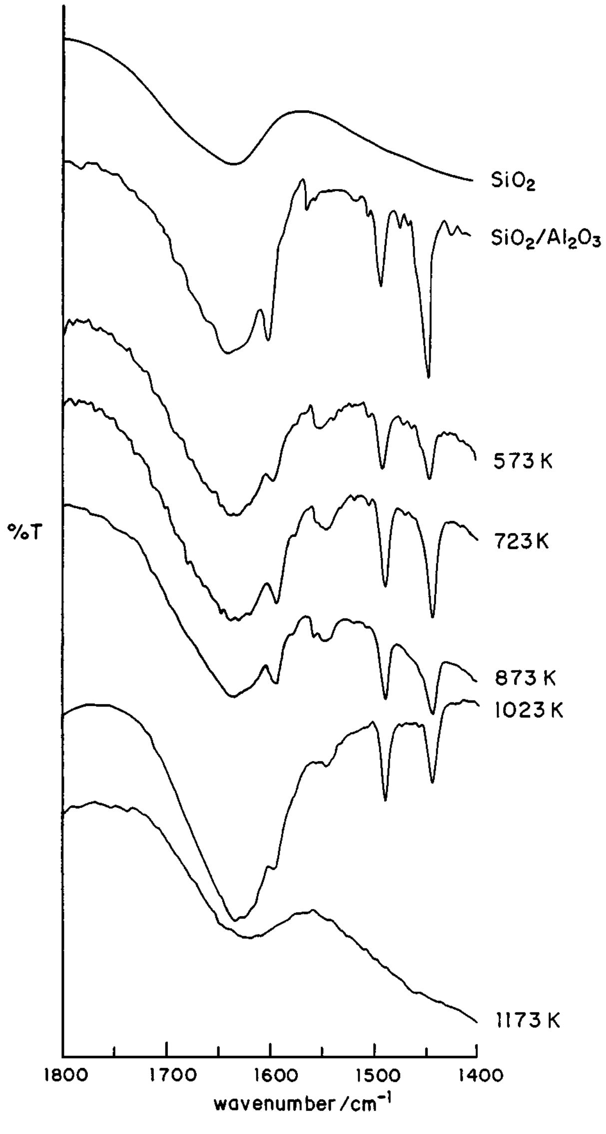

Figure 4 Infrared spectra of py adsorbed on heat treated SiO_2/Al_2O_3 at various temperatures. SiO_2/Al_2O_3 refers to the sample dried at room temperature under vacuum. SiO_2 refers to the native silica.

4. Conclusions

We have investigated the structure, thermal stability and acidity of aluminium oxide grafted on silica gel surface. We characterised by BET, XRD, XPS, NMR and DRS the fine-grained samples of SiO_2/Al_2O_3 heat treated at the temperature range of 423 to 1573 K. The specific surface areas decreased with the increase in the calcination temperature, manifesting an abrupt decrease for the sample treated at 1023 K. Above 1100 K the matrix became non-porous. DRS, using pyridine as a molecular probe, showed that the Lewis acid sites were observable for samples calcined at temperatures up to 1023 K, and for higher temperatures, the specific surface area was so drastically reduced that pyridine was not detected. The Al/Si atomic ratios measured by XPS remained approximately constant for samples heat treated at the temperature range of 423 to 1173 K, but decreased significantly for higher calcination temperatures, presumably due to the diffusion of aluminium to the matrix interior. NMR detected two species for samples calcined between 423 and 1023 K, and a third one for higher calcination temperatures, which could be associated to phase separated aluminium oxide on the surface. We concluded that the aluminium oxide was highly dispersed on the silica gel surface and it remained stable up to 1023 K.

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