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Improvement in the surface acidity of $Al_2O_3{\cdot}SiO_2$ due to a high Al dispersion

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Using ethylene glycol derivatives of aluminium isopropoxide and ethyl orthosilicate precursors in the sol–gel process, discrete aluminosilicate nanoparticles were produced that had a strong Brönsted acidity, high surface area and high thermal stability; these properties were ascribed to a high dispersion of the aluminium atoms in the silica matrix.

Acid catalysts have been the subject of considerable fundamental research, since they represent a very relevant family of solid acids that are widely utilized in the chemical and petrochemical industries.[1] In regard to catalysis, pure SiO_2 is of limited use, owing to the absence of active sites in its matrix. The substitution of Si in the SiO_2 matrix by Al, creates a negative charge on the SiO_2 framework with an associated H^+ being bound to a nearby oxygen atom to maintain charge neutrality. This results in the formation of Brönsted acid protons as Al–OH–Si bridges. One factor affecting the Brönsted acidity is the dependency on the bond angle in Si–O–Al,[2,3] while another important factor may be said to result from 'the degree of dispersion of the Al ions'. Taking account of the latter factor, in the multi-component sol–gel processes for the general preparation of aluminosilicates, it is important to control the rate of hydrolysis of the precursors. As the hydrolysis rates of the respective precursors are considerably different in the preparation of aluminosilicates gels composed of different mixtures of the elements will be formed (Al_2O_3 in the SiO_2 matrix), instead of a homogeneous hybrid material. This difficulty can be largely overcome by controlling the hydrolysis rates through the formation of more stable aluminium complexes. Zarur and Ying[4] have recently reported that an ultra-high component dispersion plays a pivotal role in the preparation of catalysts with high reactivity and thermal stability that are needed for a variety of applications. Since solid acidic catalysts are used in various catalytic reactions, it is very important to develop them to have a reproducible and strong surface acidity. In the present work, we aimed to prepare an aluminosilicate acid catalyst containing well-dispersed Al ions, and to then clarify its acidic characteristics.

Discrete nanoparticles of aluminium silicate (denoted $Al_2O_3{\cdot}SiO_2$) having well dispersed Al atoms, were prepared by mixing 0.23 mol of ethyl orthosilicate (TEOS) with aluminium isopropoxide (0.02 mol) to prepare a sample with an Si : Al ratio of 11.5. Ethylene glycol was added to this suspension, and a resultant phase-separated mixture was formed which changed to a white suspension after stirring for 1 h at 35 °C. This suspension was mixed with an aqueous NaOH solution (0.13 mol, 300 cm^3) using a spray gun to form a mist to enable the hydrolysis reaction to proceed slowly and homogeneously. The suspension was kept at 50 °C for 2 d, and then finally aged for a further 2 d at 120 °C. The sample obtained was washed well and dried in air at 35 °C and then finally calcined in an oxygen stream for 10 h at 600 °C. An acidic ZSM-5 zeolite (HZSM-5, Si : Al = 11.9) provided by the Tosoh company, and a silica–alumina sample containing 5 wt% of Al_2O_3 (denoted as SA-5) prepared by a conventional sol–gel method[6] were used as reference samples. The prepared $Al_2O_3{\cdot}SiO_2$ sample had a specific surface area of 711 $m^2\ g^{-1}$, which was larger than that of the SA-5 sample (216 $m^2\ g^{-1}$).

All ^{27}Al and ^1H MAS NMR measurements were carried out in a field of 7 T using a Varian UNITY INOVA 300 spectrometer with a 7-mm diameter zirconia rotor, filled with dry air. Before the ^1H NMR measurements, all samples were evacuated at 450 °C to eliminate any physisorbed water. Tetramethylsilane (TMS) was used as the external reference for the ^1H signals, and all the spectra were calibrated to this reference. ^{27}Al NMR spectra were measured by using a $\pi/20$ pulse and a recycle delay time of 1 s. For Al NMR measurements, all samples were evacuated at 27 °C. The ^{27}Al signals and their chemical shifts were referenced in ppm with respect to an external $Al(H_2O)_6{}^{3+}$ standard in a 1 M aqueous $Al(NO_3)_3$ solution.

The ^{27}Al MAS NMR spectra for the three samples are shown in Fig. 1. These are potentially very helpful for probing the quantity, coordination and location of aluminium atoms in aluminosilicates, even though the quadrupolar nature of the nucleus does not allow observation of the structurally significant fine structure of the bands. The $Al_2O_3{\cdot}SiO_2$ sample showed an ^{27}Al band centred at 54.6 ppm, in the region corresponding to tetrahedrally coordinated aluminium (Al^{IV}). It is notable that there is virtually no component at 0 ppm, characteristic of an aluminium ion in octahedral coordination (Al^{VI}).[5–7] The spectra of the HZSM-5 and SA-5 samples give a pattern similar to that of $Al_2O_3{\cdot}SiO_2$, with the intensity of the 54.6 ppm band largest for HZSM-5, and smallest for SA-5 among the samples used. The HZSM-5 and SA-5 samples also had a distinctive band at 0 ppm, indicating the presence of six-coordinate aluminium ions. It cannot be emphasized too strongly that this band was not observed in our $Al_2O_3{\cdot}SiO_2$ sample. These NMR results demonstrate that the Al oxide moiety was successfully incorporated into the silica framework by the present preparation method using ethylene glycol.

The resulting spectra from the ^1H MAS NMR measurements are shown in Fig. 2. The ^1H MAS NMR spectrum for HZSM-5 was composed from the sum of the contributions of the following types of OH groups: (i) SiOH at *ca.* 1.8 ppm; and (ii) SiO(H)Al at 4.2 and 6.3 ppm (the latter as a weak shoulder).[8]

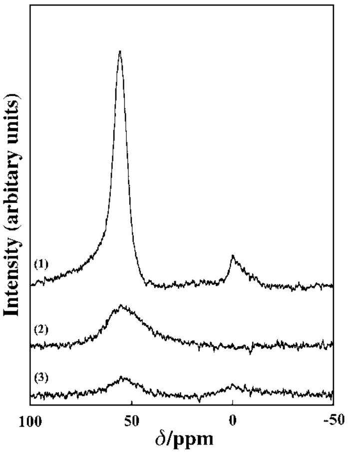

Fig. 1 ^{27}Al MAS NMR spectra for samples evacuated at 27 °C: (1) HZSM-5, (2) $Al_2O_3{\cdot}SiO_2$, (3) SA-5 samples.

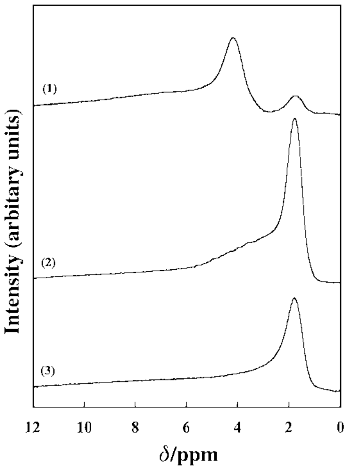

Fig. 2 ^{1}H MAS-NMR spectra for samples evacuated at 450 °C: (1) HZSM-5, (2) $Al_2O_3{\cdot}SiO_2$, (3) SA-5 samples.

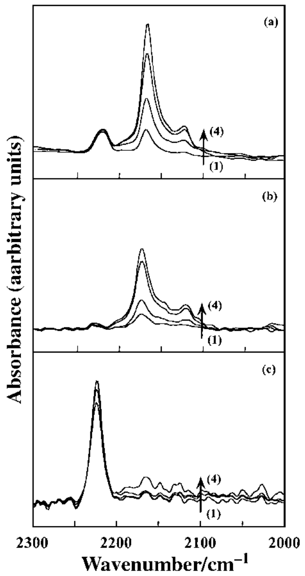

Fig. 3 FTIR spectra of CO adsorbed on the samples: (a) HZSM-5, (b) $Al_2O_3{\cdot}SiO_2$, (c) SA-5. The samples were first evacuated at 450 °C and then equilibrated with increasing pressures of CO gas at 27 °C: (1) 6.65, (2) 13.3, (3) 20.0 and (4) 26.6 kPa.

Similar to HZSM-5, a distinctive broad feature with a maximum centred around 3.8 ppm was found for the $Al_2O_3{\cdot}SiO_2$ sample, together with the emergence of an intense signal around 1.8 ppm. In contrast to these samples, the broad band was scarcely discernible for the SA-5 sample, and the band at 1.8 ppm was dominant. For the SA-5 sample, a broad band around 2.7 ppm, assigned to an AlOH species, was detected when a deconvolution technique was applied to the observed spectrum.[5,8] As a result, for the $Al_2O_3{\cdot}SiO_2$ sample, the existence of a higher number of strongly acidic Brönsted-acid sites compared to the SA-5 sample is evident, although not so strong in acid strength and in as large a quantity as those observed for the HZSM-5 sample.

It is well known that the adsorption of CO on zeolites gives rise to carbonyl stretching vibration (ν_{CO}) bands at higher wavenumber relative to the free molecule (2143 cm^{-1}), depending on the strength of interaction.[9,10] These bands are expected to be observable through the interaction of CO with Brönsted acid sites, even at room temperature. The procedure used to record the IR spectra *in situ* and the details of the sample cell used have been reported in previous papers.[5,8]

The adsorption of CO on the 450 °C-treated HZSM-5 sample at 22 °C resulted in the development of a distinct ν_{CO} band with a maximum around 2170 cm^{-1}, and its band-maximum shifted to a lower wavenumber of 2168 cm^{-1}, with a distinct shoulder toward the lower wavenumber end (Fig. 3) at a pressure of 26.6 kPa. The spectrum measured at higher pressure was deconvoluted into two components at 2170 and 2165 cm^{-1}. Another feature is the appearance of a band at 2228 cm^{-1}. It should be noted that a similar spectral pattern, except for the 2228 cm^{-1} band, was obtained for the $Al_2O_3{\cdot}SiO_2$ sample, where a strong band was found at 2170 cm^{-1}. As for the SA-5 sample, the two bands discussed for the other samples were scarcely observed, although a strong band could be seen at 2228 cm^{-1}. In addition, the FTIR spectra in the OH vibrational stretch region showed prominent band features with two components for the HZSM-5 sample, one at 3745 cm^{-1}, and the other, a broad band, at around 3620 cm^{-1}. The appearance of the band at 2170 cm^{-1} was accompanied by a shift in the OH band observed at 3620 cm^{-1}, *i.e.* an interaction with the Brönsted acid site, and the 2165 cm^{-1} band was related to an interaction with the silanol group, related to the band at 3745 cm^{-1}.[5,11] For the $Al_2O_3{\cdot}SiO_2$ sample, the IR spectrum showed a discernible shoulder at 3620 cm^{-1} at the foot of a strong band at 3745 cm^{-1}, showing a similar trend to the HZSM-5 system in this regard. On the other hand, the SA-5 sample exhibited a faint shoulder around 3620 cm^{-1}, and a strong band was observed around 3745 cm^{-1}. The strong band around 3745 cm^{-1} scarcely changed even after CO adsorption on the SA-5 sample, coinciding with the absence of a band at around 2170 cm^{-1}. Taking into account the IR and the NMR data, there is no doubt about the existence of the Brönsted acid site in the $Al_2O_3{\cdot}SiO_2$ sample; the $Al_2O_3{\cdot}SiO_2$ sample possesses a larger number of Brönsted acid sites, and a more homogeneous site distribution compared to sample SA-5.

The distinctive band at 2228 cm^{-1} arising from the adsorbed CO species as observed in the spectra of the HZSM-5 and SA-5 samples is due to the interaction of CO with strong Lewis acid sites through a σ-donor bond.[9,10] It is of note that this band does not appear for the $Al_2O_3{\cdot}SiO_2$ sample, clearly indicating the lack of a Lewis acid centre. This result corresponds well with the NMR data, which shows a lack of octahedral aluminium sites. These data are indicative of the stability of the lattice of the $Al_2O_3{\cdot}SiO_2$ sample.

In conclusion, we have shown that the preparation of an $Al_2O_3{\cdot}SiO_2$ sample utilizing ethylene glycol as a solvent, leads to a sample having a strong Brönsted acid character. The appearance of this strong acidic property is attributable to a high dispersion of aluminium atoms at the atomic level in the SiO_2 lattice, which is more complete than that observed for a sample prepared by the general sol–gel method. Utilizing the present method, we can prepare various hybrid materials that consist of elements which are well dispersed at the atomic level, and expect such highly component-dispersed materials to exhibit many applications in catalysis, adsorption technology and other areas of importance.

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