Synthesis, characterization and catalytic activity of amorphous Al,SiO$_x$ gels from weakly acidic aqueous solutions

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Al,SiO$_x$ gels have been prepared by reaction of different inorganic aluminium compounds with silicic acid. Characterization by chemical analysis, ^{27}Al MAS NMR spectroscopy and adsorption measurements shows that the gels obtained from a mixture (pH *ca.* 3) of basic aluminium chlorides and silicic acid in water are porous and contain tetrahedrally coordinated aluminium in the framework. IR spectroscopy and TPDA measurements confirm that Brønsted and Lewis acid sites are present in the gels. Finally, catalytic activity was found in hex-1-ene isomerization.

Sol–gel methods are often used for the preparation of amorphous aluminosilicates for catalytic applications[1–5] demanding acid sites *e.g.* in isopropyl alcohol dehydration[1] and in the Diels–Alder reaction of isoprene and acrylaldehyde.[5] Reactants in these sol–gel processes are organic silicon and organic aluminium compounds[1–4] and inorganic aluminium compounds,[5] respectively. The pore size of the formed gels depends on the nature of the organic additives in the reaction mixtures.[6]

During the reaction structural hydroxy groups[2] also denoted as 'bridging' groups are created by incorporation of aluminium in the SiO$_2$ network. These groups may be responsible for the catalytic activity of the resulting materials; therefore their content should be high. However, there exist difficulties in preparing amorphous aluminosilicate gels with such properties *via* the sol–gel method consisting of differences of the hydrolysis–condensation rates of the silicon and aluminium containing precursors which have to be equalized.

On the other hand aluminosilicate gels can also be obtained by continuous precipitation from a mixture of sodium aluminate solution and sodium silicate solution (water-glass).[7,8] However, to get the more catalytically active H$^+$ form of these gels, a second reaction step is necessary to exchange the sodium ions with NH$_4^+$ ions and to calcine them.

Here, we describe a new synthesis of aluminosilicate gels, hereafter referred to as Al,SiO$_x$ gels, from inorganic compounds only. The synthesis consists of a reaction of silicic acid with basic aluminium chlorides containing differently hydrolysed aluminium cations in a weakly acidic aqueous solution. Characteristic data of these gels are also given.

Experimental

Sample preparation

For the preparation of the gel samples solutions of AlCl$_3$·6H$_2$O ($c_{Al} = 0.1$ M) and basic aluminium chlorides, respectively, containing differently hydrolysed aluminium oxohydroxo cations {[Al(H$_2$O)$_6$]$^{3+}$ (Al$_{mono}$), polymeric aluminium cations[9] (Al$_{poly}$) with up to now unknown structure and tridecameric aluminium cations[10] — 'Keggin' cations — [AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$, (Al$_{13}$)} were used as Al sources. A commercial product (Locron®; OH/Al = 2.5) was chosen as basic aluminium chloride with Al$_{poly}$ cations. The basic Al$_{13}$ chloride was prepared following the procedure given in ref. 10. The aqueous solution of silicic acid ($c_{Si} = 1$ M, pH 2.3) was obtained from a diluted sodium silicate solution ($c_{Si} = 2$ M, Na/Si ≈ 0.6) by ion exchange (ion-exchange resin KPS 200; H$^+$ form). The freshly prepared silicic acid was aged for 1 h before use.

The gels were prepared by reaction of aluminium cations with silicic acid (Si/Al = 5) in a weakly acidic medium (pH 2.7–3.2). The transparent solutions stored at room temperature became gels after times between a few minutes and some days depending on the aluminium compound used. The gels were washed with distilled water free of chloride and dried at 353 K. The NH$_4^+$ and Na$^+$ forms of the samples were obtained by treatment with 1 M NH$_4$Cl and 1 M NaCl solution, respectively, at 363 K. Some gels were calcined at 713 K for 2 h.

The gel samples prepared from various reactants and under different conditions are listed in Table 1.

Instrumentation

Usual gravimetric methods were used for the determination of the chemical compositions of the samples.

Table 1 Preparation and Si/Al ratios of Al, SiO$_x$ gels

gel	Al source	Si/Al ratio[a]	ion exchange	calcination temp./K
1	Al$_{mono}$	33.4	—	—
2	Al$_{mono}$	11.4	—	—
3	Al$_{poly}$	5.1	—	—
3-C			—	713
3-NH$_4^+$			NH$_4$Cl	—
3-NH$_4^+$/C			NH$_4$Cl	713
3*	Al$_{poly}$	5.8	—	—
3*-Na$^+$			NaCl	—
4	Al$_{13}$	5.3	—	—
4-C			—	713
4-NH$_4^+$			NH$_4$Cl	—
4-NH$_4^+$/C			NH$_4$Cl	713
4*	A$_{13}$	6.1	—	—
4*-NH$_4^+$			NH$_4$Cl	—
4*-Na$^+$			NaCl	—
5	Al$_{mono}$	14.5	—	—
6	Al$_{poly}$	5.0	—	—
7	Al$_{13}$	5.4	—	—

[a]Of washed gels.

The ^{27}Al MAS NMR investigations were carried out on a Bruker MSL 400 spectrometer at a resonance frequency of 104.2 MHz with a spinning rate of 12 kHz. The nitrogen adsorption isotherms were obtained by means of the automated gas adsorption system ASAP 2000M (Micromeritics). The surface area and pore diameter of the gels were calculated by the BET and BJH methods.

For temperature-programmed desorption of ammonia (TPDA), NH_3 was adsorbed at 393 K on samples activated at 393 and up to 873 K. After flushing with He at 393 K for 2–3 h, NH_3 desorption was initiated by heating at a rate of 10 K min^{-1} to 873 K in a He flow of 0.5 cm^3 s^{-1}. The NH_4^+ forms of the samples were only flushed with He at 393 K before TPDA was started. The desorbed amount of NH_3 was determined continuously in a thermal conductivity cell and integrally by adsorption in a trap containing 0.05 M sulfuric acid followed by titration with a NaOH solution. IR spectra were recorded at room temperature in the ranges 3800–3200 cm^{-1} and 1800–1200 cm^{-1} by an M85 Specord Instrument (Carl Zeiss Jena) using self-supporting wafers. The samples were placed in a quartz IR cell and activated by heating to 673 K under vacuum. To remove any physically adsorbed molecules evacuation at room temperature was carried out after the adsorption of ammonia at room temperature. Stepwise desorption of ammonia was carried out from room temperature to 753 K.

The isomerization of hex-1-ene at 373 K as a catalytic test reaction was performed in a conventional, atmospheric pressure laboratory flow system with hydrogen as carrier gas. The feed flow rates were 25 cm^3 min^{-1} at 25 °C yielding space velocities of 250 cm^3 g^{-1} min^{-1} with feed molar ratios of hex-1-ene to H_2 of 0.057. A HP 5890/II gas chromatograph with a flame ionization detector was used for analysis of reaction products. Before the catalytic reaction, the samples were pretreated at 473 K in hydrogen flow.

Results and Discussion

Chemical composition

At first the effects of the used different Al sources (Al_{mono}, Al_{poly}, Al_{13}), of the SiO_2 concentrations and of the pH of the reaction mixtures on the composition (Si/Al ratio) of the prepared Al,SiO_x gels were studied. The results are summarized in Table 2.

Upon mixing Al_{mono} with silicic acid in a Si/Al molar ratio of 5 a transparent solution (pH = 1.6) is obtained which became a gel after 14 days (gel 1). As shown in Table 2 its aluminium content is small. This means that probably no reaction takes place between the silicic acid and the hexaaquoaluminium cations $[Al(H_2O)_6]^{3+}$, an observation which confirms the findings of other authors.[11,12]

The preparation of the gels 2 and 5 was performed in a similar way but by adding a solution of 0.3 M aqueous ammonia to the acidic reaction mixture up to a pH of 2.9. The aluminium content of these gels is also low, but higher than in gel 1. It is supposed that in this case a small quantity of aluminium oxohydroxo cations formed by hydrolysis during the addition of ammonium hydroxide solution reacts with the silicic acid. This is due to the fact that by using Al_{poly} and Al_{13}, respectively, as aluminium sources the Si/Al ratios of the starting solutions (= 5) and the resulting gels 3, 4, 6 and 7 (Table 2) are not different from each other which hints at a reaction of these aluminium cations with the silicic acid. As it follows from Table 2 the gelation time depends on the nature of the aluminium cations and the SiO_2 concentration in the starting solutions; the time varies between a few minutes and several weeks. A reason for this observation may be a varied behaviour of the different aluminium oxohydroxo cations concerning their destruction in a stronger acid solution. The basicity (OH/Al ratio = 2.5) and the pH (4–5) of both the Al_{poly} and Al_{13} containing solutions are the same. By adding silicic acid to the Al_{poly} or Al_{13} solutions the pH value falls to 2.9–3.2. Under these acidic hydrolysis conditions low molecular mass aluminium fragments with reactive OH groups may be formed from Al_{poly}/Al_{13} which react with the silicic acid building units to connect them *via* Al—O—Si bonds. In the case of Al_{13} gelation occurs after few minutes (gels 4, 7); by using Al_{poly} the time to gelation is longer (up to several days, gels 3, 6). That means that the formation of reactive aluminium species under the conditions of hydrolysis is faster for Al_{13} than Al_{poly}. By comparison a pure 0.3 M silicic acid polymerizes into silica gel after 14 days.

Table 2 Synthesis and ^{27}Al MAS NMR results of Al,SiO_x gels

		starting solution[a]			Al,SiO_x gels	
gel	Al source	c_{Si}/mol l^{-1}	pH	gel time	Si/Al ratio[b]	^{27}Al MAS NMR Al^{IV}/Al^{VI} (%)
1	Al_{mono}	0.57	1.6	14 d	33.4	64/36
2	Al_{mono}	0.30	2.90	6 d	11.4	79/21
3	Al_{poly}	0.30	2.85	28 h	5.1	54/46
4	Al_{13}	0.30	3.20	9 min	5.3	66/34
5	Al_{mono}	0.09	2.95	> 12 w[c]	14.5	64/36
6	Al_{poly}	0.09	2.85	3 d	5.0	50/50
7	Al_{13}	0.09	3.10	13 min	5.4	73/27

[a]Si/Al = 5. [b]Of washed gels. [c]After 12 weeks the water was removed by distillation.

To obtain information on the structure, acidic properties and catalytic activity of Al,SiO_x gels prepared as above they were characterized by ^{27}Al NMR spectroscopy, adsorption measurements, IR spectroscopy, TPD of ammonia and hex-1-ene isomerization as a catalytic test reaction. The results are given below.

^{27}Al NMR spectroscopy

Fig. 1(a) shows the ^{27}Al NMR spectrum of the solution prepared by mixing Al_{mono} with silicic acid after a reaction time of 21 h. Only one signal at 0 ppm is observed which is assigned to octahedrally coordinated aluminium (Al^{VI}) in Al_{mono}.[14] The solid-state spectrum of the gel formed from this solution after 14 days [Fig. 1(b)] shows also only one signal at 0 ppm. These results confirm that SiO_2 and possibly $AlCl_3 \cdot 6H_2O$ $\{[Al(H_2O)_6]Cl_3\}$ exist in the gel side-by-side and thus no reaction of the components with formation of Al—O—Si bonds has taken place (pH < 2).

After washing the gel subsequently with water the Si/Al ratio rises from 5 to 33.4 (Table 2) and an additional signal at 53 ppm is observed in the ^{27}Al MAS NMR spectrum [Fig. 1(c)]. This signal is due to tetrahedrally coordinated aluminium (Al^{IV}) which is linked *via* oxygen bridging atoms with silicium.[15] Obviously during the washing protolysis of $Al(H_2O)_6{}^{3+}$ cations occurs leading to partial formation of aluminium oxohydroxo species which react with terminal silanol groups of the silica. The change of the Si/Al ratio indicates that the aluminium chloride is removed from the gel by washing and 64% of the remaining aluminium in the gel occurs in tetrahedral coordination as estimated from the signal intensities in Fig. 1(c) (Table 2, gel 1). The compensation of the negative charges in the gel caused by the incorporation of Al probably takes place by protons and/or aluminium cations containing Al^{VI}. This is supported by the fact that a certain amount of octahedrally coordinated Al cannot be removed by washing [36% of the remaining Al; Fig. 1(c), Table 2].

Fig. 2(a) shows the ^{27}Al MAS NMR spectrum of gel 3 (Table 2) which was prepared from Al_{poly} and silicic acid as an example of gels synthesized using Al_{poly} or Al_{13}. It should

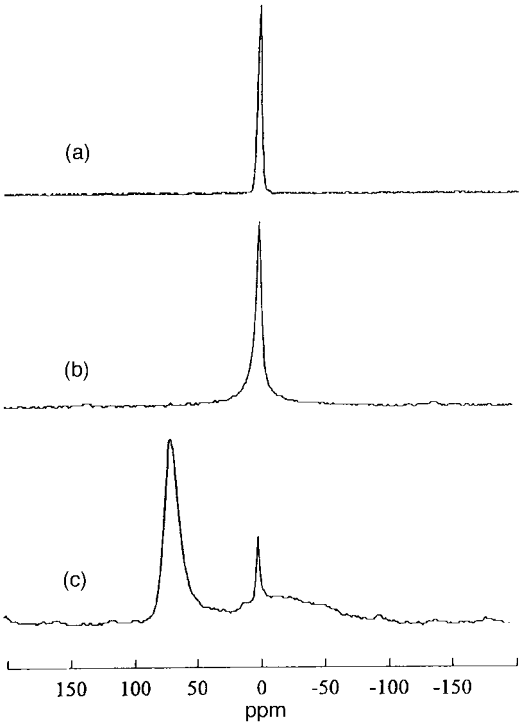

Fig. 1 ^{27}Al NMR spectra of (a) starting solution containing Al$_{mono}$ and silicic acid after 21 h (pH = 1.6), (b) unwashed and (c) washed gel (gel 1)

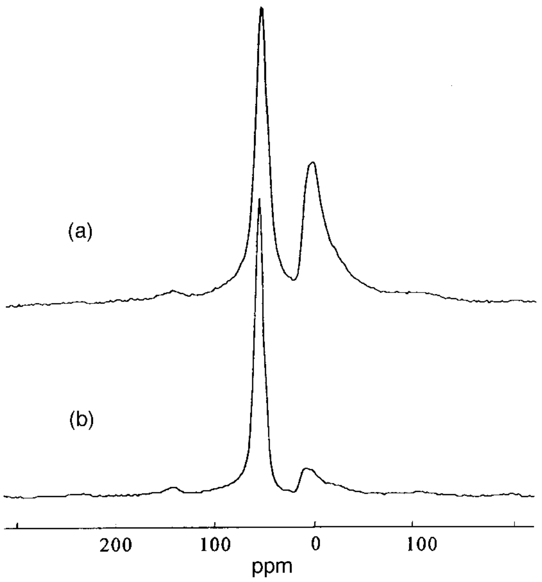

Fig. 2 ^{27}Al MAS NMR spectra of gel 3 before (a) and after (b) NH$_4^+$ exchange

be noted that in such gels the Si/Al ratio does not change with washing. The presence of both signals at 54 and 0 ppm in the spectra of the unwashed as well as the washed gel 3 dried at 353 K demonstrates that both tetrahedrally (Al^{IV}) and octahedrally (Al^{VI}) coordinated aluminium exist in the product;† from the signal intensities the calculated amount of Al^{IV} in the washed gel is 54%.

Table 3 Ion exchange and ^{27}Al MAS NMR results of Al,SiO$_x$ gels

Al source	gel	Si/Al ratio	time of ion exchange/h	^{27}Al MAS NMR Al^{IV}/A^{VI} (%)
Al$_{poly}$	3	5.1		54/46
	3-NH$_4^+$		7	75/25
	3-NH$_4^+$		49	84/16
	3*	5.8		50/50
	3*-Na$^+$		7	65/35
Al$_{13}$	4	5.3		66/34
	4-NH$_4^+$		7	100/0
	4*	6.1		70/30
	4*-NH$_4^+$		7	96/4
	4*-Na$^+$		49	82/18

To obtain information regarding the nature of the Al^{VI} in the gels they were treated in an ion-exchange process with 1 M NH$_4$Cl solution. From the NMR spectrum in Fig. 2(b) and Table 3 (gel 3, gel 3-NH$_4^+$) it can be seen that the amount of Al^{VI} is reduced by the exchange process (49 h). In gel 4 prepared from Al$_{13}$ and silicic acid practically no Al^{VI} is detectable after the ion-exchange process (7 h). These results support the assumption that the negative charges formed by the incorporation of aluminium in the silica framework are at least partially balanced by aluminium cations (Al^{VI}). It can be assumed that the better interchangeability of the Al^{VI} in the gels prepared from Al$_{13}$ and silicic acid is connected with both the structure of the gels and the nature of the aluminium cations. The cations are expected to be of lower molecular mass compared with those in the gels prepared from Al$_{poly}$ and silicic acid.

In connection with questions regarding the acidity and the catalytic activity, respectively, of the gels discussed below, ion-exchange with 1 M NaCl solution was also studied. ^{27}Al MAS NMR results of such treated gels (gel 3*-Na$^+$, gel 4*-Na$^+$)‡ are listed in Table 3 together with those for the gels 3*, 4* and 4*-NH$_4^+$. It becomes evident by comparison of the relative signal intensities of the spectra of gel 3*-Na$^+$ and gel 3*-NH$_4^+$ that by exchange (7 h) with sodium chloride solution less octahedrally coordinated Al (*ca.* 30%) is removed than by exchange with NH$_4^+$ cations (*ca.* 46%). This effect was also observed for the gel 4* whereas during the treatment with NH$_4$Cl solution virtually all the Al^{VI} is exchanged. After exchange with NaCl solution 18% Al^{VI} remains in the gel although the time of the exchange process was extended (49 h).

Adsorption measurements

The influence of Al$_{poly}$ and Al$_{13}$, respectively, on the pore size distribution of the gels was investigated by measuring the nitrogen adsorption isotherms.

Fig. 3 and 4 show isotherms for the gels 3 and 4, for the gels ion-exchanged with NH$_4^+$ (3-NH$_4^+$, 4-NH$_4^+$) and for samples calcined at 713 K (2 h) (gels 3-C, 4-C).

The course of the adsorption isotherm of the gel 3 hints at a microporous solid, whereas for gel 4 a continuous increase of the isotherm in the high-pressure branch is observed which indicates the existence of additional mesopores in the gel. Accordingly a higher amount of mesopores can be calculated from the corresponding BET and BJH surfaces, respectively, for gel 4 prepared from Al$_{13}$ and silicic acid than for gel 3 (Table 4). The figures and also the results listed in Table 4 show further that calcination leads to a decrease of the adsorption capacity of *ca.* 40% (gel 3-C, gel 4-C).

Regarding possible influences of the ion-exchange process on parameters of the gels such as specific surface area, *etc.* it can be stated that only for the gel prepared from Al$_{poly}$ and silicic acid does ion exchange with NH$_4$Cl lead to an increase of the adsorption capacity (gel 3-NH$_4^+$); simultaneously the

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† A similar spectrum is obtained for gel 4 prepared from Al$_{13}$ and silicic acid. The absence of the signal at 62.5 ppm characteristic for Al^{IV} in Al$_{13}$ cations is evidence for the destruction of these Al cations in a more strongly acidic solution as discussed earlier.

‡ The gels denoted by * refer to a second synthesis run of the gels 3 and 4 (see Table 1).

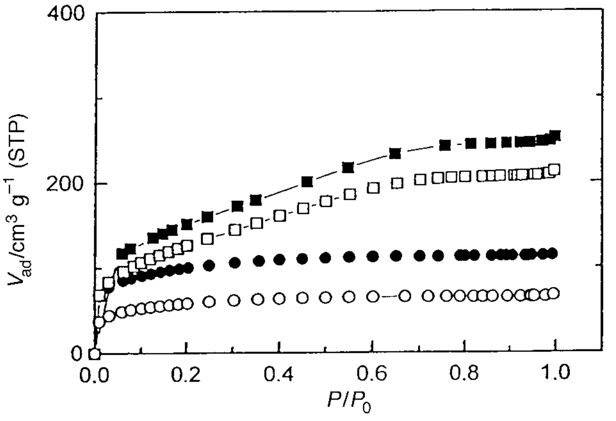

Fig. 3 Adsorption isotherms of nitrogen at 77 K: (●) gel 3, (○) gel 3-C, (■) gel 3-NH_4^+, (□) gel 3-NH_4^+/C

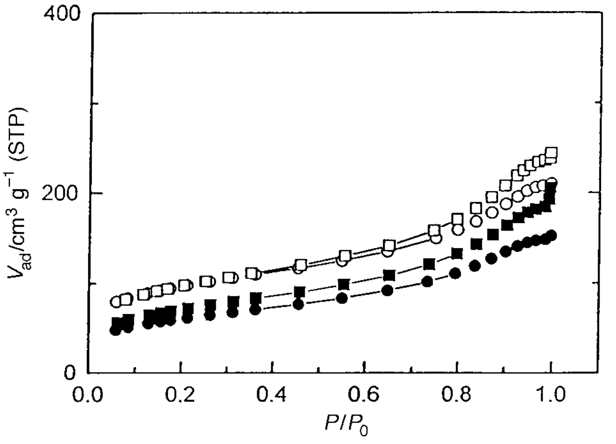

Fig. 4 Adsorption isotherms of nitrogen at 77 K: (○) gel 4, (●) gel 4-C, (□) gel 4-NH_4^+, (■) gel 4-NH_4^+/C

mesoporous character increases (Table 4). This is also illustrated by the shape of the isotherm of gel 3-NH_4^+ in the region of higher pressures (Fig. 3); the effect is also observed after calcination (gel 3-NH_4^+/C).

A comparison of the pore size distributions of gel 3 and gel 3-NH_4^+ (Fig. 5) also reflects the differences with respect to adsorption capacity and pore sizes caused by ion exchange of the sample. In gel 3-NH_4^+ an additional pore volume for the adsorption of N_2 molecules may become accessible because of removal of some of the probably more highly condensed aluminium cations. In contrast to that, for gel 4 prepared from Al_{13} and silicic acid, ion exchange does not lead to a significant change of the porous structure; this points to the existence of low condensed aluminium cations which can be easily exchanged by NH_4^+ cations (Fig. 6, Table 4). From comparison of the pore volume distribution curves shown in Fig. 5 and 6 and from the mean pore size (Table 4) of gels 3 and 4 it is seen that gels prepared from Al_{13} and silicic acid contain larger pores than the gels synthesized with Al_{poly}. Therefore it can be postulated that the clearly better exchangeability of the aluminium cations in the gel prepared from Al_{13} and silicic acid is connected with the larger pore sizes compared with those of gel 3.

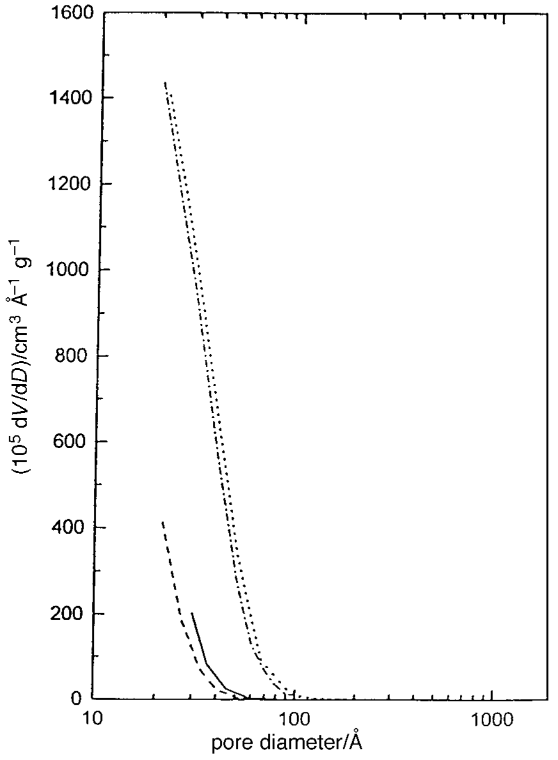

Fig. 5 Distribution of pore diameter: (—) gel 3, (– – –) gel 3-C, (...) gel 3-NH_4^+, (–·–·–) gel 3-NH_4^+/C

Specific surface areas and mean diameters of pores of gels 3* and 4* which were prepared in a comparable way from Al_{poly} and Al_{13}, respectively, and silicic acid, are listed in Table 4. It is seen that the quantity of mesopores is larger in gel 3* compared with gel 3. Differences in relation to mesopores are also observed for gels 4 and 4* synthesized from Al_{13} and silicic acid. This indicates that the pore size distribution, especially the formation of micropores and mesopores of these types of gels, can be influenced by small variations of the synthesis procedure or the pre-treatment of the gel samples.

Table 4 Surface area and pore diameter of Al, SiO_x gels

		surface area/$m^2\ g^{-1}$		average pore diameter/Å	
Al source	gel	BET	BJH (17–3000 Å)	BET ($4V/O_{BET}$)	BJH ($4V/O_{BJH}$)
Al_{poly}	3	349	110	26	30
	3-C	206	66	20	26
	3-NH_4^+	544	414	28	33
	3-NH_4^+/C	461	382	28	32
	3*	339	229	21	23
Al_{13}	4	341	194	38	54
	4-C	218	151	42	56
	4-NH_4^+	346	227	43	57
	4-NH_4^+/C	255	183	45	59
	4*	290	129	27	41
	4*-NH_4^+	273	131	28	40

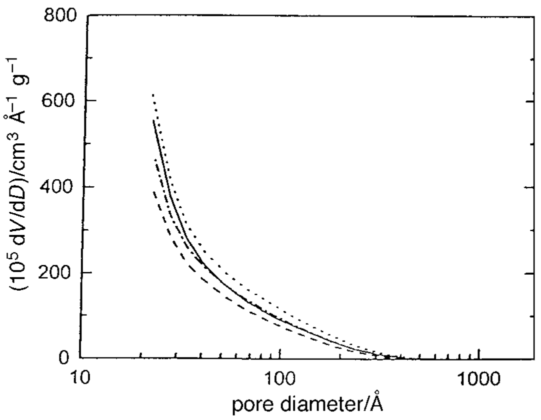

Fig. 6 Distribution of pore diameter: (—) gel 4, (– – –) gel 4-C, (...) gel 4-NH_4^+, (–·–·–) gel 4-NH_4^+/C

A further reason for the observed differences may be the higher SiO_2 content in the gels 3* and 4*, respectively (Table 1).

IR spectroscopy

Fig. 7 shows the IR spectra of the gels 3 and 4* in the region of the OH-stretching vibrations. Bands at 3740 and 4550 cm^{-1} are attributed to the stretching and combination tone vibrations of SiOH groups. The weak band observed at 3620 cm^{-1} can be regarded as evidence for acidic bridging hydroxy groups (Brønsted sites) in the gel samples like in crystalline aluminosilicates.[2,17,18] This finding is in accordance with the results of NMR measurements. Tetrahedrally coordinated aluminium as identified by ^{27}Al MAS NMR spectroscopy verifies the presence of Al—O—Si bonds which are responsible for the bridging hydroxy groups. The octahedrally coordinated aluminium also detected by NMR could be the origin of the Lewis acid sites.

To gain further information about the nature of the acid sites of the gels they were investigated by using NH_3 as a probe molecule. Since the IR spectra of gels 3 and 4*, prepared from Al_{poly} and Al_{13}, respectively, show no differences, only those of gel 3 are discussed here as an example. Fig. 8 shows IR difference spectra of gel 3 after ammonia adsorption and following desorption in the temperature range 323–753 K.

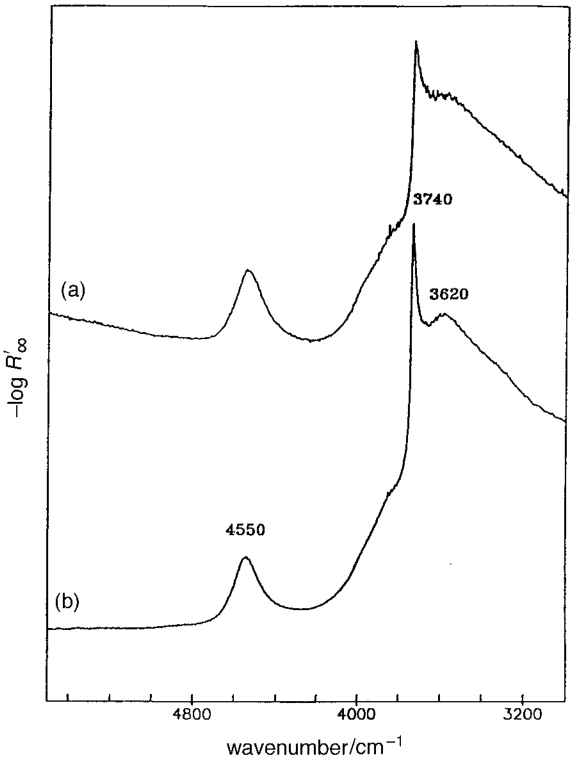

Fig. 7 IR OH vibration spectra of gel 3 (a) and gel 4* (b)

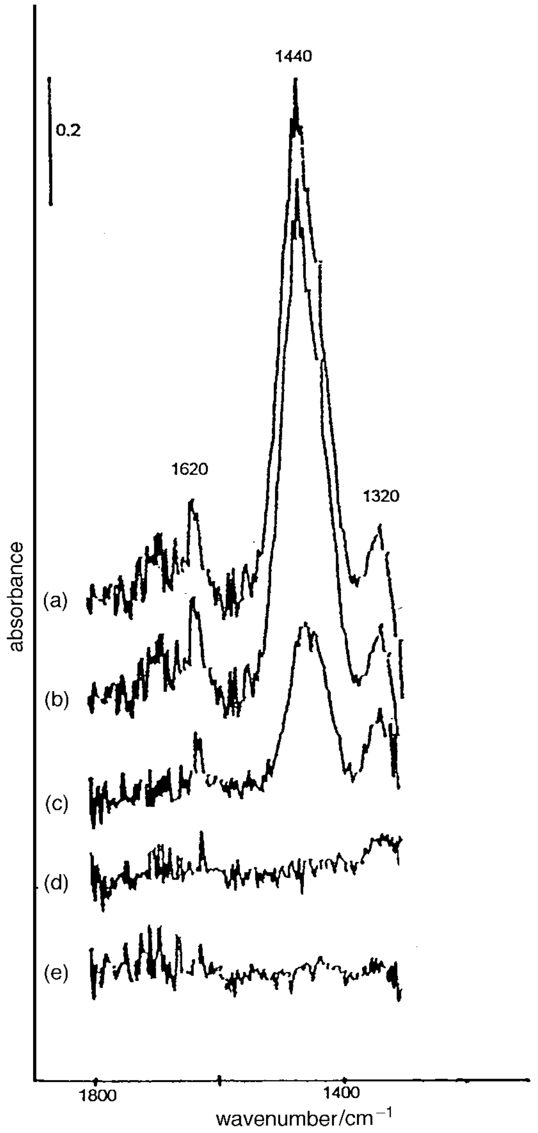

Fig. 8 IR difference spectra of gel 3 after adsorption of ammonia, following desorption at 323 K (a), 373 K (b), 473 K (c), 673 K (d) and 753 K (e)

The band at 1440 cm^{-1} (δ NH_4^+) is assigned to NH_4^+ arising from interaction of the protons of the acidic OH groups (Brønsted sites) with NH_3.[19] Bands at 1620 and 1320 cm^{-1} ($\delta_{as,s}$ NH_3) are attributed to coordinatively bound NH_3 (Lewis sites). As can be seen in Fig. 8 and Table 5 the intensity of the bands decreases with increasing desorption temperature. At

Table 5 NH_3 adsorption and desorption of gel 3

	relative intensities of the IR bands	
temperature of desorption/K	NH_4^+ (1440 cm^{-1})	NH_3 (1320 cm^{-1})
323	0.80	0.13
373	0.78	0.13
473	0.25	0.10
573	0.04	0.10
673	—	0.04
753	—	0.03

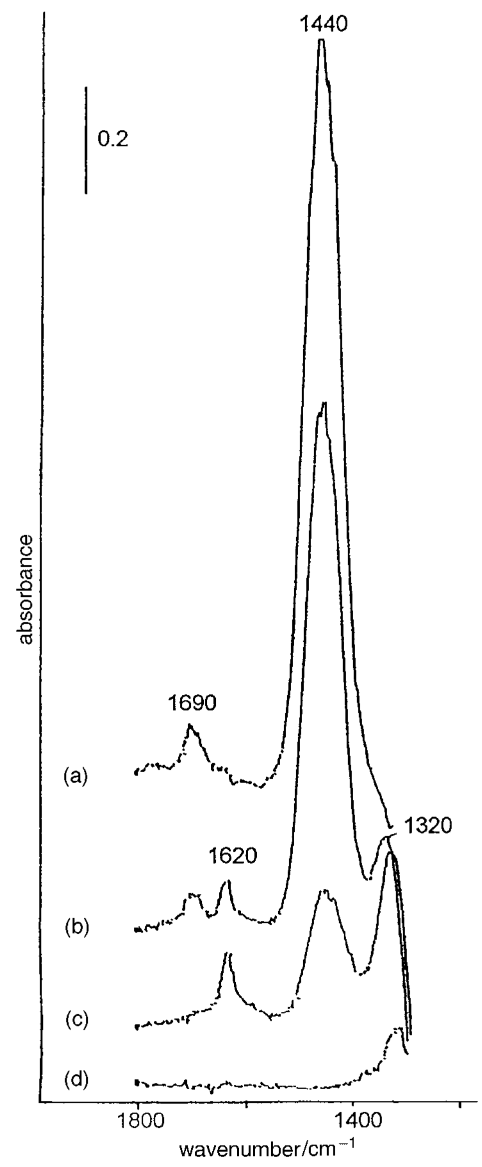

Fig. 9 IR difference spectra after stepwise thermal decomposition of gel 4*-NH_4^+ at 423 K (a), 473 K (b), 573 K (c) and 673 K (d)

673 K the band at 1440 cm^{-1} disappears completely whereas the band at 1320 cm^{-1} is reduced in intensity but still detectable at 753 K. The results clearly demonstrate that the gels contain both medium strength Brønsted sites and Lewis sites. Since the desorption temperatures for the coordinatively bound ammonia are a measure of the acid strength the results given in Table 5 show that gel 3 contains Lewis acid sites ranging from weak to strong. The IR spectra after stepwise thermal decomposition of the NH_4^+ forms of the gels are shown for gel 4*-NH_4^+, as an example, in Fig. 9. They are characterized primarily by bands at 1690 and 1440 cm^{-1} ($\delta_{s,as}NH_4^+$) which are assigned to NH_4^+ ions in the positions of Brønsted sites formed during the exchange of protons§ and of aluminium cations by ammonium ions. These bands are still visible after desorption at 423 K [Fig. 9(a)] but decrease with increasing desorption temperature and disappear between 573 and 673 K, caused by thermal decomposition of NH_4^+ and release of NH_3. Simultaneously new bands arise at 1620 and 1320 cm^{-1} related to coordinatively bound ammonia which is formed by the interaction of the released ammonia with Lewis sites. IR investigation on gel 3-NH_4^+ showed the same results. It should be noted that these strong acid Lewis sites do not necessarily occur primarily in the as-formed gels and may well be created upon change of the gel structure at higher temperatures as a consequence of partial dealumination with formation of Al^{VI}. Such behaviour was observed, for example, for gels 3 and 4* upon precalcination in vacuum at 673 K.

TPD of ammonia

To characterize the acid sites of the gels in detail their behaviour in TPD of ammonia (TPDA) was studied. TPDA results for gels 3 and 4* are given in Fig. 10(a) and Table 6. The low-temperature peak indicates the presence of weak acid sites whereas the high-temperature peak is due to strong acid sites. Furthermore, it is evident that in the gel 4*, prepared from Al_{13} and silicic acid, the amount of strong acid sites is higher (94.5%) than for gel 3 (83.8%) from Al_{poly}. This result seems to be a consequence of the higher percentage of tetrahedrally coordinated aluminium as found by ^{27}Al MAS NMR measurements for gel 4* (Table 3).

The decomposition of gel 4*-NH_4^+ under TPDA conditions is compared with the TPDA curve of gel 4* in Fig. 10(b). Comparison of the two curves suggests that the high-temperature peak predominantly corresponds to Brønsted sites.

To obtain information about the thermal stability, TPDA measurements were carried out after sample calcination at temperatures between 393 and 873 K in an inert gas (He) atmosphere. As can be seen by the results given in Fig. 11 and Table 7 the acidity is very strongly diminished upon heat treatment, especially in the region of the Brønsted acid sites owing to dehydroxylation reactions at higher temperatures.

Simultaneously a broadening of the low-temperature peak is observed, *i.e.* the number of weak Lewis acid sites is enhanced

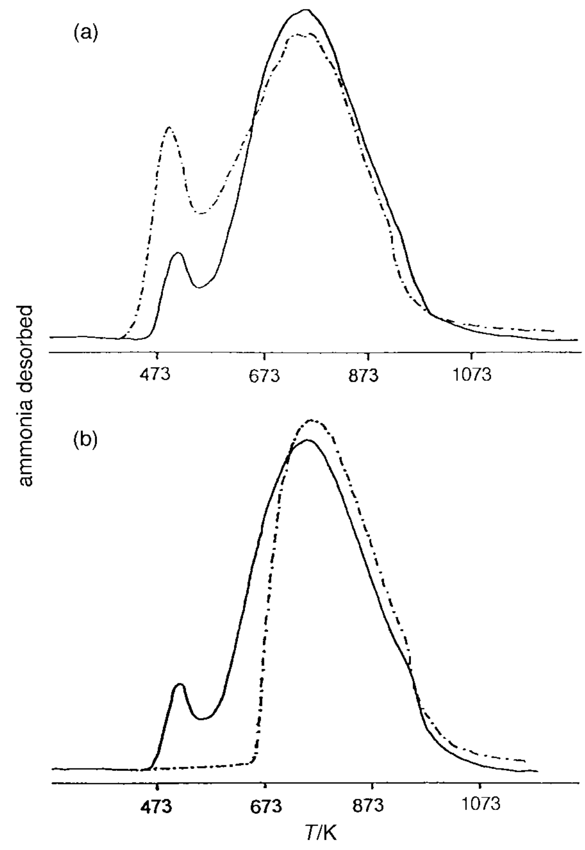

Fig. 10 TPDA curves (a) of gel 3 (–·–·–) and gel 4* (—) and (b) of gel 4* (—) and gel 4*-NH_4^+ (–·–·–)

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§ The occurrence of Brønsted sites confirms the presence of bridging hydroxy groups in the gels, *i.e.* the compensation of the negative charges of the aluminosilicate framework is partly realized by protons.

Table 6 Results of TPD of ammonia

Al source	gel	total amount of desorbed NH_3/ mmol g^{-1}	low-temperature peak desorbed NH_3/ mmol g^{-1}	high-temperature peak desorbed NH_3/ mmol g^{-1}
Al_{poly}	3	1.69	0.27	1.41
	$3\text{-}NH_4^+$	1.01	0	1.01
	3*	1.47	0.18	1.29
	$3^*\text{-}Na^+$	1.15	0.20	0.95
Al_{13}	4*	1.51	0.08	1.42
	$4^*\text{-}NH_4^+$	1.16	0	1.16
	$4^*\text{-}Na^+$	0.85	0.12	0.73

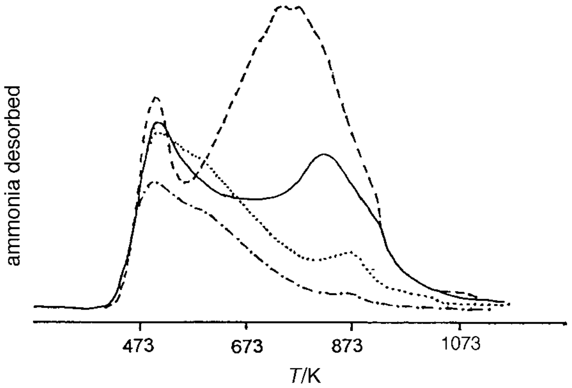

Fig. 11 TPDA: gel 3 after thermal treatment in a stream of He at 393 K (---), 573 K (—), 737 K (...) and 873 K (–·–·–)

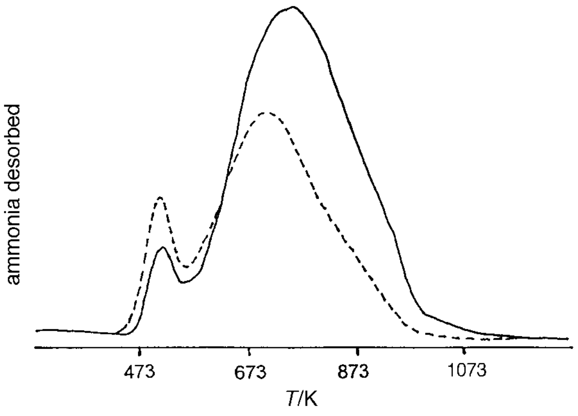

Fig. 13 TPDA curves of gel 4* (—) and gel $4^*\text{-}Na^+$ (---)

Table 7 TPD of ammonia: dependence of the acid strength of gel 3 on the temperature of calcination

temperature/K	thermal treatment/h	total amount of desorbed NH_3/ mmol g^{-1}
393	2	1.69
573	1	1.05
573	5	0.95
773	0.5	0.78
873	0.5	0.49

up to temperatures of 773 K. After thermal treatment at 873 K only 30% of the starting acidity is detected.

As shown in Fig. 12 and Table 7 the concentration and distribution of the acid sites at 573 K is only slightly influenced by extension of thermal treatment to 5 h; *i.e.* the acidity of gel 3 does not decrease significantly with time at this temperature. From this observation it can be concluded that the acidity of gel 3 is stable up to 573 K.

The TPDA curves of gel 4* and the corresponding Na^+ form are plotted in Fig. 13. It is evident from the figure and from the TPDA results given in Table 6 also for gel 3 and its Na^+ form that the concentration of the Brønsted sites (high-temperature peak) decreases upon ion exchange. The diminution of the strong acid sites amounts to 50% (gel 4*) and 30% (gel 3), respectively.

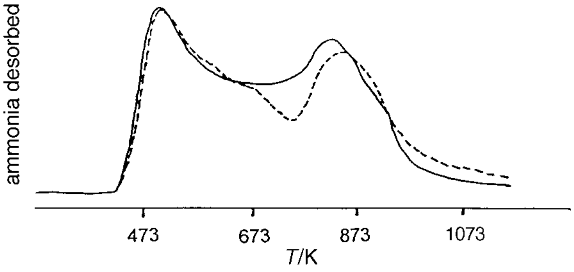

Fig. 12 TPDA of gel 3 after thermal treatment at 573 K: 1 h (—) and 5 h (---)

Catalytic activity

The catalytic test reaction used was the double bond shift isomerization of hex-1-ene. This reaction was chosen because of the low temperature required so avoiding diminution of acid sites occurring at higher temperatures in this investigation. To examine the identity of the active acid sites in this reaction the Na^+ forms of the gels were also tested; they contain less strong acid sites than the as-synthesized gels, as described above.

The results of hex-1-ene isomerization are shown in Fig. 14(a) and (b). The main products of this reaction are *cis*- and *trans*-hex-2-ene, whereas hex-3-ene appears only as a minor component. The yields of the main products are displayed as a function of reaction time.

The gels prepared from Al_{poly} (Table 1) exhibit different catalytic activities depending on the type of exchanged cations [Fig. 14(a)]. The reaction rates on gel 3* and gel $3\text{-}NH_4^+$ drop rapidly with increasing time on stream, while the rate on the gel $3^*\text{-}Na^+$ is almost constant and shows high conversion. Considering the course of activity–time curves the initial activities of all three samples seem to be almost the same. Obviously, the differences in catalytic behaviour are mainly caused by the decay of catalytic performance with reaction time.

The results obtained with the samples prepared from Al_{13} are shown in Fig. 14(b). For the gels $4^*\text{-}Na^+$ and 4* a stable and relatively high catalytic performance is found whereas for the gel $4\text{-}NH_4^+$ a rapid deactivation occurs. Similarly to the gels from Al_{poly} the initial activity of all three gels from Al_{13} is approximately the same. The differences in activity–time correlations can be attributed to differing degrees of catalyst deactivation, as for the other gels.

The rapid decrease in catalytic activity of the NH_4^+ form in both sets of experiments can be attributed to the creation

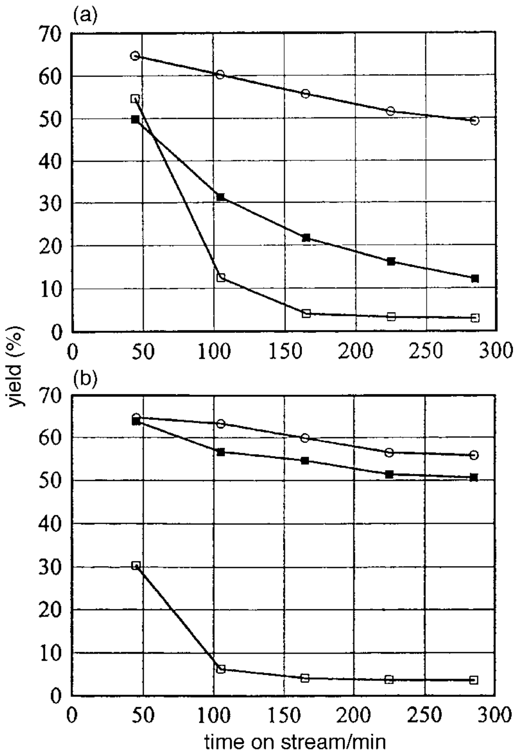

Fig. 14 Catalytic hex-1-ene isomerization on (a) gel 3* (■), gel 3*-Na^+ (○) and gel 3-NH_4^+ (□) and (b) gel 4* (■), gel 4*-Na^+ (○) and gel 4*-NH_4^+ (□)

of strong acid sites by thermal decomposition of the ammonium ions generating ammonia and Brønsted acid sites, as is well documented for NH_4-ZSM-5.[20]

In both series of gel samples the Na^+ form displays the best stability with the time on stream. The relatively high stability may be attributed to the decrease of Brønsted acidity due to Na^+ exchange and thus a reduction of deactivation rate.

The acidity of the Na^+ gels is still sufficient to isomerize hex-1-ene. Higher acidities occurring in the as-synthesized gels promote the generation of more carbonaceous deposits blocking the active sites. The decay rate of catalytic activity for the as-synthesised forms of the gels lies between those of the NH_4^+ and Na^+ forms and suggests acidity lying between both forms under reaction conditions.

The as-synthesised form as well as the Na^+ form of the gels appear to be efficient catalysts, at least for reactions occurring over weaker acid sites. The possibility of ion exchange creates the possibility to tune the acidity of these catalysts so optimising activity and reducing deactivation.

Conclusions

Al,SiO_x gels with a Si/Al ratio of 5–6 could be synthesized using silicic acid and solutions of basic aluminium chlorides, containing the oxohydroxo cations Al_{poly} and Al_{13}, respectively, in a weakly acid medium whereas by using solutions of $AlCl_3 \cdot 6H_2O$ with Al_{mono} cations $\{[Al(H_2O)_6]^{3+}\}$ at a pH value of 1.6 practically no aluminium is incorporated into the silica framework.

^{27}Al MAS NMR results show that the silicic acid has reacted with Al_{poly} and Al_{13}, respectively, with formation of Al—O—Si bonds; up to 70% of the aluminium is tetrahedrally coordinated in the gel framework. The portion of the octahedrally coordinated aluminium can be reduced by an ion exchange with NH_4^+ and Na^+, respectively.

By means of adsorption measurements it is established that the gels contain micro- and meso-pores. With heat treatment the adsorption capacity decreases as a result of dehydroxylation reactions.

From the IR results it can be concluded that the gels prepared from silicic acid and Al_{poly} and Al_{13}, respectively, contain both Brønsted and Lewis sites. The existence of strong and weak acid sites in the Al,SiO_x gels was also shown by the TPDA investigations. As a consequence of calcination at higher temperatures the concentration of acid sites decreases strongly.

The observations regarding isomerization of hex-1-ene over Al,SiO_x gels demonstrate that these substances, at least, effectively catalyze hydrocarbon reactions demanding weaker acid sites. In addition, it could be shown that the cation exchange has a strong influence on the catalyst's decay and in consequence on the performance.

The investigations have shown an alternative method to synthesize porous Al,SiO_x gels with acid properties from inorganic compounds in a weakly acidic medium.

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References

1 T. Lopez, M. Asomoza and R. Gomez, *J. Non-Cryst. Solids*, 1992, **147/148**, 769.
2 S. Rouanet, R. J. Willey and J. B. Peri, *Sol–Gel Processing and Applications*, ed. Y. A. Attia, Plenum Press, New York, 1994, p. 285.
3 G. Bellussi, C. Perego, A. Carati, S. Preatello, E. Previde Massara and G. Perego, *Stud. Surf. Sci. Catal.*, 1994, **84**, 85.
4 M. Toba, F. Mizukami, S. Niwa, T. Sano, K. Maeda and H. Shoji, *J. Mater. Chem.*, 1994, **4**, 1131.
5 Y. Matsumoto, K. Mita, K. Hashimoto and T. Tokoroyama, *Appl. Catal.*, 1995, **131**, L1.
6 S. D. Jones, T. N. Pritchard and D. F. Lander, *Microporous Mater.*, 1995, **3**, 419.
7 K. P. Wendlandt, H. Bremer, M. Jank, M. Weber, P. Starke and D. Müller, *Acta Phys. Chem.*, 1985, **31**, 35.
8 B. M. De Witte, P. J. Grobet and J. B. Uytterhoeven, *J. Phys. Chem.*, 1995, **99**, 6961.
9 R. Bertram, W. Geßner, D. Müller, H. Görz and S. Schönherr, *Z. Anorg. Allg. Chem.*, 1985, **525**, 14.
10 S. Schönherr, H. Görz, D. Müller and W. Geßner, *Z. Anorg. Allg. Chem.*, 1981, **476**, 188.
11 I. Jaymes and A. Douy, *J. Eur. Ceram. Soc.*, 1996, **16**, 155.
12 M. Fukuoka, Y. Onoda, S. Inoue, K. Wada, A. Nukui and A. Makishima, *J. Sol–Gel Sci. Tech.*, 1993, **1**, 47.
13 B. M. De Witte, K. Aernouts and J. B. Uytterhoeven, *Microporous Mater.*, 1996, **7**, 97.
14 D. Müller, D. Hoebbel and W. Geßner, *Chem. Phys. Lett.*, 1981, **84**, 25.
15 G. Engelhardt and D. Michel, *High-resolution NMR of Silicates and Zeolites*, Wiley, Chichester, 1987.
16 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1991, ch. 1.
17 N. Y. Topsoe, K. Pedresen and E. Derouane, *J. Catal.*, 1981, **70**, 41.
18 P. A. Jacobs and R. von Ballmoos, *J. Phys. Chem.*, 1982, **86**, 3050.
19 A. A. Davydov, *Infrared spectroscopy of adsorbed species on the surface of transition metals oxides*, John Wiley & Sons, 1990, p. 26.
20 U. Kürschner, H.-G. Jerschkewitz, E. Schreier and J. Völter, *Appl. Catal.*, 1990, **57**, 167.

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