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Catalysis Today 101 (2005) 131–138

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IR and NMR studies of mesoporous alumina and related aluminosilicates

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Abstract

The synthesis of mesoporous alumina and aluminosilicates of Si/Al from 0.2 to 10 was done, and the status of Si and Al was followed by ^{29}Si and ^{27}Al MAS NMR. The properties of acid sites were studied by following the IR spectra of CO, N_2, pyridine and ammonia adsorbed. The mesoporous alumina contained only surface weak Lewis acid sites, the insertion of Si resulted in loss on such Lewis sites and in the formation of Brønsted sites. The Al–OH bands decreased (the Al^{IV}–OH band related to tetrahedral Al species diminished the first) and Si–OH–Al one (IR band at 3605 cm^{-1})—similar as in the case of zeolites appeared as well as Si–OH groups (IR band at 3740 cm^{-1}). The aluminosilicates of higher Si content contained also strong Lewis acid sites formed by the dehydroxylation of Si–OH–Al groups (process similar as in zeolites), which occurred at the activation. The concentration of both Lewis and Brønsted sites was determined by quantitative IR studies of ammonia and pyridine adsorption. The concentration of Brønsted acid sites increased with Si content due to the formation of acidic Si–OH–Al, and at high Si/Al, it increases also due to the growing surface area. The concentration of Lewis sites decreased with Si content due to the transformation of surface Al species, which are potential Lewis sites into Si–OH–Al and also to dilution of the material with Si species. The acid strength of Lewis sites increased with Si content due to increasing contribution of strongly acidic sites produced by dehydroxylation. The mesoporous aluminosilicate (Si/Al = 10) studied in this research showed higher concentration and higher acid strength of Brønsted sites than HMCM-41 of the same Si/Al—it may be an potential catalyst in fine chemistry reactions.

Keywords: IR spectroscopy; NMR spectroscopy acidity; Mesoporous alumina

1. Introduction

The discovery of a new family of mesoporous silicas (M41S) [1,2] with controlled mesoporosity and uniform pores in the range from 2 to 50 nm has opened a new area of their use as catalysts and supports. However, apart from narrow pore distribution and very high surface area (usually above 1000 m^2/g), meso-SiO_2 posses only very weak acid centres (silanol groups) [3–5], which considerably limits application of such material for catalytic purposes. The generation of the acid function can be achieved by the incorporation of aluminum into the framework of mesoporous silica either by a direct surfactant synthesis [6–8] or a post-synthesis modification [9], nevertheless it is difficult to prepare materials with a considerable amount of Al in the silica framework.

The synthesis of other mesoporous metal oxides, which could be used in catalysis, has become recently object of intensive research [10,11]. A particular attention has been paid to the preparation of stable mesoporous alumina, the amorphous analogues of high surface area and excellent mechanical properties are commonly used as catalysts and catalysts supports. Mesoporous Al_2O_3 synthesized in the presence of micellar aggregates is characterized by presence of uniform regular pores and its BET surface area is usually above 400 m^2/g [12–16]. Such material could be a potential candidate for the application as a new, effective catalyst support [17–20]. On the other hand, doping mesoporous alumina with silicon atoms could be a way to prepare meso-aluminosilicates possessing acidic properties, which would make possible their catalytic use.

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doi:10.1016/j.cattod.2005.01.010

A new method of synthesis of stable mesoporous alumina and related materials using cetyltrimethylammonium bromide (CTABr) as a surfactant in water/triethanolamine (TEA) medium was reported by Cabrera et al. [21,22]. This method enables to prepare meso-aluminosilicates in a wide range of the Si/Al ratio, i.e. both aluminum rich samples ($Si/Al < 1$) obtained by doping meso-Al_2O_3 with silicon, and aluminum poor preparations ($Si/Al > 1$) containing Si as the main component. In our previous paper we have shown that such materials were thermally stable and did not loose their mesoporosity during the calcination at 520 °C [23]. On the other hand the ^{27}Al and ^{29}Si MAS NMR data have revealed that high temperature treatment caused a partial removal of Al from the structure of the mesoporous aluminosilicate and the extent of the 'dealumination' depends on the composition of the calcined material being the most significant for the mesoporous alumina and the preparations of a high Al content.

In the present contribution detailed results on the acidity of meso-Al_2O_3 and a series of mesoporous aluminosilicates with the Si/Al ratio ranging from 0 to 10, measured by adsorption of pyridine, ammonia, carbon monoxide and nitrogen and monitored with FT-IR spectroscopy, are reported. The role of the chemical composition on the nature, number and strength of acid sites formed during the post-synthesis thermal treatment and activation procedures are also discussed.

2. Experimental

2.1. Samples preparation

The synthesis of mesoporous alumina was carried out in hydrothermal conditions at 393 K for 72 h, according to the published recipe [21], in the system:

$$(Al_2O_3)_1(CTABr)_1(TEA)_{15}(Na_2O)_{0.25}(H_2O)_{110s}$$

using following reactants: aluminum *sec*-butoxide (Merck), triethanolamine (Fluka), cetyltrimethylammonium bromide (Fluka), sodium hydroxide (POCh) and water.

The syntheses of the mesoporous aluminosilicates (SA) were carried out by the same 'cationic surfactant route' using TEA as a complexing agent, which enables one to control the process of hydrolysis and condensation of aluminum and silicon containing species [22]. Irrespectively of the chemical composition of the gel, all syntheses were carried out at room temperature for 48 h. Tetraethylorthosilicate (TEOS), aluminum *sec*-butoxide (Merck), triethanolamine (Fluka), cetyltrimethylammonium bromide (Fluka), sodium hydroxide (POCh) and water were used as reactants and syntheses were performed for several different Si/Al ratios. The obtained samples are labeled as SA(X), where $X = 0.2$, 0.5, 1, 5, and 10 is the Si/Al ratio in the synthesis gel. The obtained mesostructured materials were washed with hot water, recovered by centrifugation and dried using freeze-drying procedure. The molecules of the surfactant trapped in the pores of synthesized materials were removed by calcination in argon at 793 K for 8 h (heating rate 1 K/min) and subsequently in dry air at the same temperature also for 8 h. The calcined mesoporous materials contain Na^+ cations balancing the charge introduced into the framework by the $Si–O^-–Al$ species. The transformation of the Na^+ form of mesoporous alumina and aluminosilicates into the NH_4^+ one was carried out by an ion-exchange procedure at 333 K using an excess of concentrated aqueous solution of NH_4NO_3. The sodium content in the exchanged samples was below 0.3 wt.%.

HMCM-41 ($Si/Al = 10$) was the same as used in our previous study [24]. We used also partially dehydroxylated H-Ferrierite the same as investigated in our previous study [25]. This ferrierite has been calcined at vacuum at 920 K for 1 h.

2.2. XRD

The as-synthesized and calcined mesoporous materials were characterized by X-ray powder diffraction. The XRD patters were recorded using Siemens 5005 powder diffractometer with Cu-Kα radiation (50 kV, 30 mA), 0.001° step size and 2 s step time.

2.3. SEM

The morphology and the size of the particles of synthesized samples were determined with scanning electron microscope (Philips 30 XL).

2.4. BET

The BET surface area and mesoporosity were checked by the nitrogen adsorption isotherms (Quantochrome NOVA 2000 sorptiometer) of the samples activated at 573 K for 3 h prior the measurement.

2.5. NMR

^{27}Al and ^{29}Si MAS NMR was applied to study the state of Al and Si atoms in the mesoporous materials under study. The ^{29}Si MAS NMR spectra were measured on Bruker AMX360 spectrometer (magnet 360 MHz, ^1H NMR frequency) using custom-built MAS probe with 7 mm o.d. rotor (spinning speed approximately 5 kHz). ^{29}Si MAS NMR single pulse spectra were recorded at 71.5 MHz frequency, with a 3.5 (90°) pulse and a 30 s relaxation delay. The ^{27}Al MAS NMR spectra were measured in a 500 MHz frequency magnet (Bruker AMX500 spectrometer) with a 10° pulse. About 0.2 s relaxation time and a 12 kHz rotation speed using homemade probehead with 3.5 mm o.d. rotor. ^{27}Al frequency was 130.3 MHz. The samples were kept at 75% relative humidity for 48 h prior to the experiments.

2.6. Sorption studies

The nature, number and strength of acid sites were determined by adsorption of pyridine, ammonia, carbon monoxide and nitrogen after activation of the samples in vacuum (10^{-6} mbar) at 723 K for 1 h using a temperature increment of 10 K/min. The samples were prepared as self-supporting discs and placed inside IR cell. The spectra were recorded on Equinox 55 Bruker spectrometer with a resolution of 2 cm^{-1} and normalized to the 10 mg of sample.

3. Results and discussion

Mesostructured materials were obtained for all the gel compositions. The SEM analysis showed, that meso-alumina and aluminosilicates formed irregular blocks, which consisted of small (about 1 μm in diameter) particles. The X-ray patterns were poorer than for purely siliceous MCM-41 solids, indicating the loss of the characteristic hexagonal pore ordering. They featured a main peak centered in the range between 50 and 62 Å for all the as-synthesized samples. Transmission electron microscope (TEM) analysis confirmed the XRD data and showed no order in the pore arrangement (disordered hexagonal or sponge like pore distribution). An estimation of pore diameters, made from XRD and porosity data gave similar values of about 38–40 Å and indicated that the wall thickness increased with Al content.

The high temperature surfactant removal did not result in loose of the mesoporosity. The BET surface area of the calcined samples increased from 490 (for mesoporous alumina) to 1220 m^2/g for silica rich preparation (SA = 10) (Table 1).

3.1. The formation of acid sites

3.1.1. IR studies of CO adsorption

The IR spectra of CO adsorbed at 170 K on Al_2O_3, on aluminosilicates of various Si/Al, as well as on purely siliceous MCM-41 are presented in Fig. 1. The spectra of CO adsorbed on H-Ferrierite are presented as well. Partially dehydroxylated (calcined at 920 K) H-Ferrierite has been chosen as a reference system, because it contains several kinds of acid sites: bridging Si–OH–Al (IR band at 2173 cm^{-1}), two kinds of weak Lewis acid sites being extraframework Al species (2192 and 2208 cm^{-1}), as well as two kinds of strong Lewis acid sites produced by dehydroxylation (2220 and 2230 cm^{-1}).

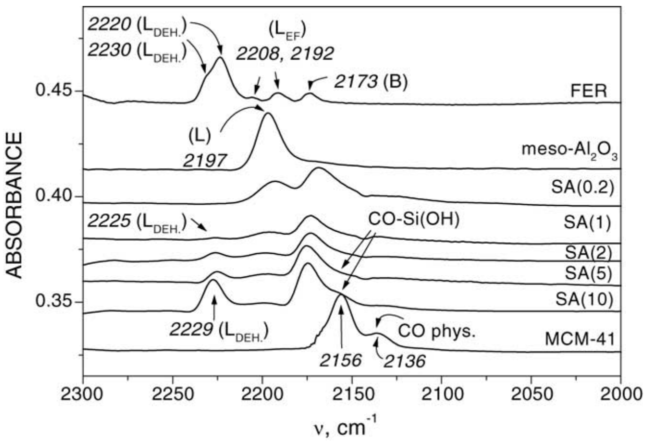

Fig. 1. IR spectra of CO adsorbed at 170 K on H-Ferrierite, mesoporous Al_2O_3, aluminosilicates of various Si/Al (from 0.2 to 10) and on mesoporous purely siliceous MCM-41.

The spectrum of CO adsorbed on MCM-41 (Fig. 1) shows the bands of physisorbed CO (2136 cm^{-1}), and of CO bonded to silanol Si–OH groups by hydrogen bonding (2156 cm^{-1}). The spectrum of CO adsorbed on Al_2O_3 shows one distinct band at 2197 cm^{-1} of CO bonded to Al species being weak Lewis acid sites. The insertion of tetrahedral Si into Al_2O_3 results in the decrease of the amount of such Al species. The 2197 cm^{-1} decreases and shifts a little to lower frequency. The frequency shift is the best seen in Fig. 2 in which the spectra of CO adsorbed on Al_2O_3 and on aluminosilicate of Si/Al = 0.2 (SA (0.2)) are presented again, and the difference spectrum is given as well. Comparing the positions of IR bands of CO shows, that Lewis acid sites in Al_2O_3 represented by CO band at 2197 cm^{-1} are inhomogeneous: the most electroacceptor Al species (represented by negative band at 2198 cm^{-1} seen in difference spectrum) were removed first if

Table 1
The surface area (*S*), concentration of Brønsted (B) and Lewis (L) sites measured by pyridine and ammonia sorption

Sample	*S* (m^2 g^{-1})	Concentration of acid sites							Strength of acid sites			
		Pyridine (μmol g^{-1})		NH_3 (μmol g^{-1})		NH_3 (μmol m^{-2})		NH_3 (μmol g^{-1})	NH_3 ($A_{des.}/A_0$)		Pyridine ($A_{des.}/A_0$)	
		B	L	B	L	B/S	L/S	(B + L)Al	B	L	B	L
Al_2O_3	490	0	440	0	930	0	1.9	0.05	–	0.39	–	0.58
SA (0.2)	680	80	430	190	920	0.29	1.35	0.07	0.46	0.38	0.34	0.74
SA (1)	470	150	400	290	640	0.61	1.36	0.09	0.73	0.44	0.39	0.74
SA (2)	540	200	450	370	620	0.68	1.14	0.15	0.68	0.41	0.52	0.80
SA (5)	750	230	460	470	605	0.63	0.81	0.32	0.64	0.50	0.45	0.82
SA (10)	1220	210	400	530	370	0.43	0.30	0.50	0.55	0.70	0.54	0.89
HMCM-41	1250	140	380	335	230	0.29	0.25	0.32	0.45	0.59	0.50	0.65

The concentration of acid sites per 1 m^2 of surface area (B/S and L/S) and the amount of acid sites (B + L)/1 Al atom (B + L)/Al.

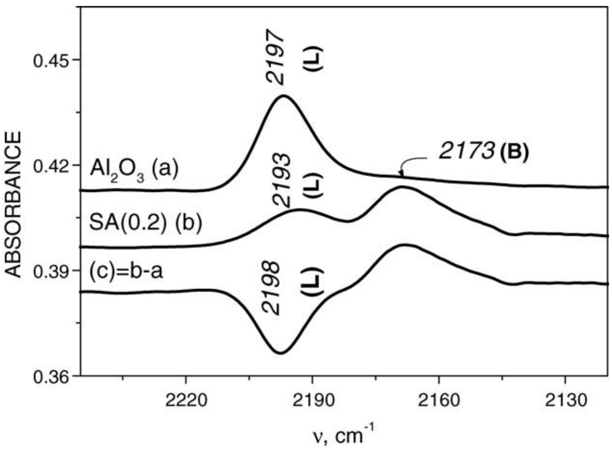

Fig. 2. IR spectra of CO adsorbed on (a) Al_2O_3, (b) SA (0.2) and (c) difference spectrum c = b − a.

Si is inserted, and less electroacceptor ones (represented by 2193 cm^{-1} band) remained.

The insertion of Si (Fig. 1) resulted in the appearance of 2170 cm^{-1} band of CO bonded to Brønsted acid sites, i.e. Si–OH–Al groups. In the case of aluminosilicates of Si/Al $\geq$ 1 a CO band at 2225 cm^{-1} is present. This band is typical of strong Lewis acid sites produced by the dehydroxylation of bridging hydroxyls, similar to those formed by the dehydroxylation of zeolites. However, in the case of aluminosilicates there is only one kind of such strong Lewis sites, whereas in zeolites two kinds of such strong acid sites are present (CO bands at 2220 and 2230 cm^{-1}). According to the data presented in Fig. 1, the intensity of 2225 cm^{-1} band increases with Si content, what is probably due to the fact, that the amount of Brønsted acid sites increases, and higher density of such bridging hydroxyls facilitates the dehydroxylation. This band shifts also to higher frequency (up to 2229 cm^{-1}) indicating the increase of acid strength of such Lewis sites.

Changes in the nature of the Lewis sites observed for the samples with different Si/Al ratios result from their different behavior at high temperatures. It has been shown [19] that the high temperature treatment applied to remove the occluded molecules of the surfactant and to decompose the NH_4 form prior to the measurements results in a partial elimination of Al atoms from the mesoporous solids. The extent of the Al removal depends on the chemical composition of the sample and was proved [23] to be considerably higher for the Al rich materials. Changes in the average chemical shift of the ^{29}Si MAS NMR as a function of the post-synthesis treatment of the aluminum rich SA (0.2) and silicon rich samples SA (2) and SA (5) are presented in Fig. 3. The shift of the line position – in respect to the ^{29}Si resonance line of the as-synthesized material – of the calcined and ion-exchanged samples towards the negative edge of the spectrum. This points to a process of the Al removal from the environment of the Si atoms. The highest shift observed for SA (0.2) (8.8 ppm) materials confirms a lower thermal stability of this aluminosilicate and an easier formation of the extraframework Al species when compared to the samples containing SiO_2 as a main component (1.9 ppm, for SA (5) sample).

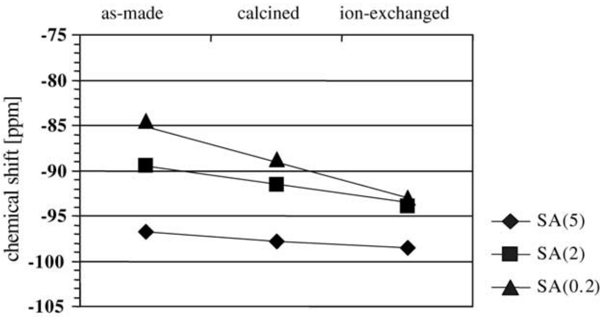

Fig. 3. Plot of the average chemical shift of the ^{29}Si NMR NMR spectrum as a function of the chemical composition of a sample and its post-synthesis treatment.

3.1.2. OH groups in aluminosilicates

The IR spectra of OH groups on the surface of mesoporous Al_2O_3, and aluminosilicates of various Si/Al are presented in Fig. 4. The spectrum of Al_2O_3 shows 5 OH

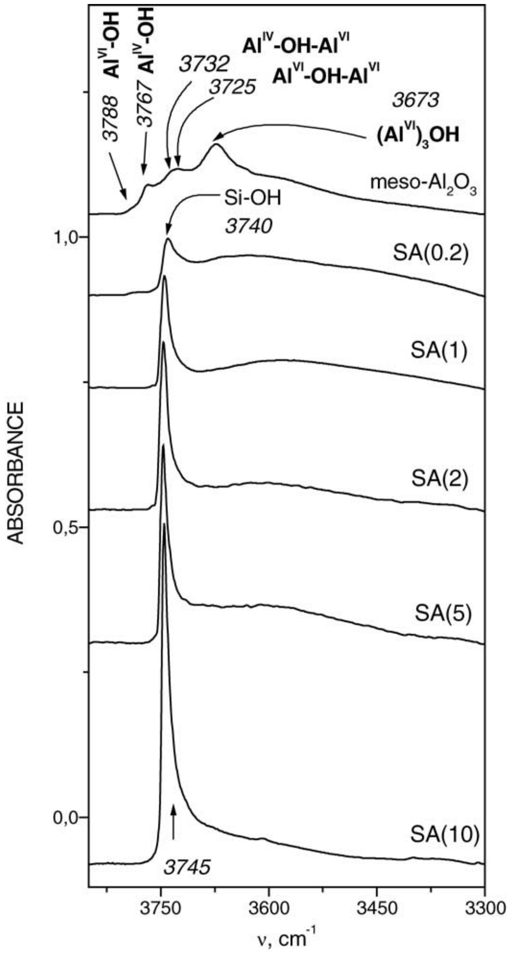

Fig. 4. IR spectra of OH groups on Al_2O_3, and aluminosilicates of various Si/Al.

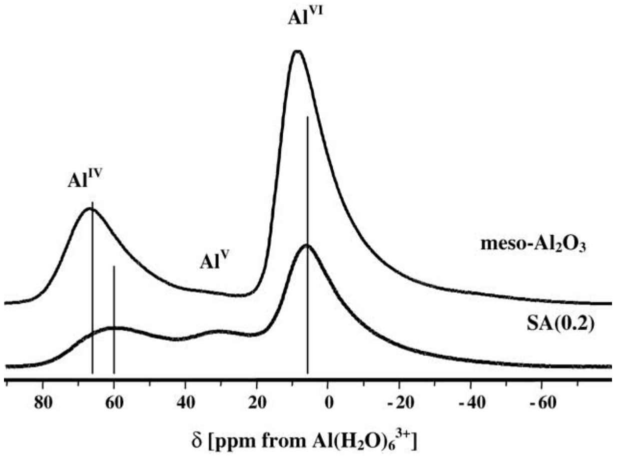

Fig. 5. ^{27}Al MAS NMR spectra of meso-Al_2O_3 and SA (0.2).

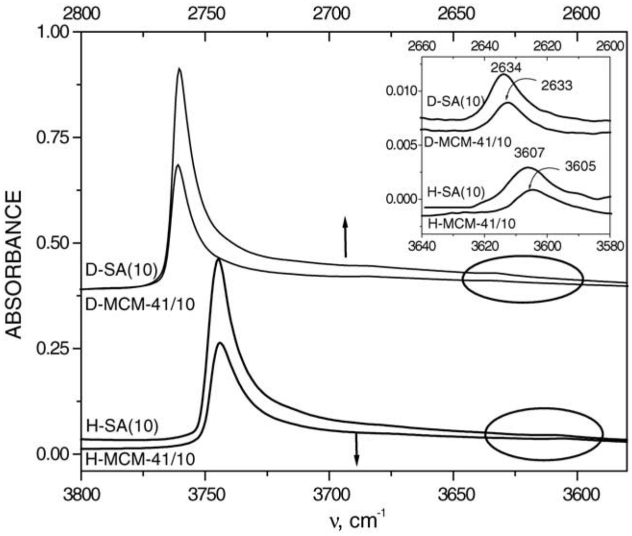

Fig. 6. IR spectra of OH groups in SA (10) and HMCM-41 (Si/Al = 10) and of OD groups in deuterated materials.

bands, the assignment of which has been proposed by Knözinger and Ratnasamy [26]. The band at 3767 has been assigned to isolate Al^{IV}–OH groups bonded to tetrahedral Al (type Ia), the band at 3788 cm^{-1} to isolate Al^{VI}–OH bonded to octahedral Al (type Ib), the bands at 3725, 3732, and 3673 cm^{-1} to bridging Al^{IV}–OH–Al^{VI} (type IIa), Al^{VI}–OH–Al^{VI} (type IIb), and to bridging $(Al^{VI})_3OH$ (type III). It should be noted, that ^{27}Al MAS NMR studies evidenced the presence of tetrahedral Al in calcined mesoporous Al_2O_3 (Fig. 5).

The insertion of tetrahedral Si into mesoporous Al_2O_3 results in the decrease of Al–OH bands and in appearance of Si–OH one (at 3740 cm^{-1}). The bands due to isolated Al^{IV}–OH at 3767 and 3789 cm^{-1} are removed in the first order. This IR result correlates with the result of ^{27}Al MAS NMR studies. The ^{27}Al MAS NMR spectra of the mesoporous alumina and the aluminosilicate doped with a small number of Si atoms are compared in Fig. 5. All the Al signals decrease when Si is present in the sample, but the signal of the tetrahedral Al (at 70 ppm) decreases the most when the first Si atoms are inserted and a new signal at about 58 ppm appears. This indicates changes in the chemical environment of the tetrahedrally coordinated Al atoms (at Si/Al = 0.2) caused by the replacement of Al^{IV}–OH groups by Al^{IV}–OH–Si. At Si/Al > 1 there is no more Al–OH groups, only Si–OH band is present. If a homogeneous Al and Si distribution is assumed, each Al is surrounded by Si atoms and there is no possibility to form Al–OH groups.

In zeolites, the bridging Si–OH–Al groups being Brønsted acid sites are characterized by IR band at 3550–3660 cm^{-1}. The position of the IR band depends on the acid strength (the frequency decreases with the acid strength). The OH frequency is also lowered by the interaction of hydrogen atom with framework oxygens across the channel (this is especially important in the zeolites of narrow pores). The spectrum of our aluminosilicate of Si/Al = 10 is presented in Fig. 6. A very weak but well visible band at 3607 cm^{-1} of Si–OH–Al is seen, besides of a strong band of silanol groups at 3740 cm^{-1}. As the IR spectrum may contain some very narrow vibration – rotation bands of atmospheric water, which may produce artifacts, the spectrum of OD groups in deuterated samples was also recorded (Fig. 6). The OD bands appear in 2600–2700 cm^{-1} region, which is free of the problems of atmospheric water and in which the sample transition is better than in the typical OH region (3600–3700 cm^{-1}). A weak Si–OD–Al band at 2634 cm^{-1} is well seen also in the spectrum of deuterated sample. As far as we know the spectra presented in Fig. 6 are the best visualization of bridging Si–OH–Al (or Si–OD–Al) groups in aluminosilicates not being crystalline zeolites. Even though amorphous aluminosilicates contained considerable amounts of Brønsted acid sites (detected by pyridine adsorption), it was very difficult to observe the OH band (around 3600–3610 cm^{-1}), due to low value of extinction coefficient of weakly acidic hydroxyls.

3.2. *The properties of acid sites studied by pyridine and ammonia adsorption*

The IR spectra of pyridine adsorbed on alumina and aluminosilicates are presented in Fig. 7. In the case of alumina only the bands of pyridine bonded to Lewis acid sites at 1450, 1614 and 1621 cm^{-1} are present. The insertion of Si results in the formation of Brønsted acid sites (IR bands at 1545 and 1635 cm^{-1}). The frequencies of the band of pyridine bonded to Lewis sites increase with Si content, indicating the increase of the acid strength. This may be related to partial dehydroxylation of Brønsted sites (Si–OH–Al groups), what produces strongly electroacceptor sites. This is also seen in the spectra of adsorbed CO (Fig. 1) in which the intensity of the band of CO bonded to strongly acidic Lewis sites does also increase with Si content.

The concentration of Brønsted and Lewis acid sites was determined in quantitative IR studies of pyridine and

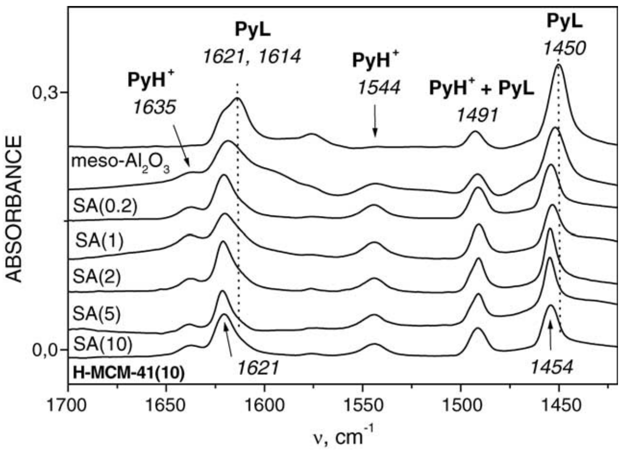

Fig. 7. IR spectra of pyridine adsorbed at 420 K on Al_2O_3, on aluminosilicates of various Si/Al and on HMCM-41 (Si/Al = 10).

ammonia adsorption. The excess of pyridine and ammonia (sufficient to neutralize all the acid sites) was adsorbed at 420 K, and physisorbed molecules were subsequently removed by the evacuation at the same temperature. The concentration of Brønsted and Lewis acid sites was calculated from the intensities of 1545 and 1450 cm^{-1} bands (for PyH^+ and NH_4^+, respectively) and of 1450 and 1620 cm^{-1} bands (for PyL and NH_3L, respectively), by using the extinction coefficients of these bands. The values of extinction coefficients were determined in the experiments in which the measured portions of pyridine or ammonia were adsorbed in H-Mordenite (containing only Brønsted acid sites) or on Al_2O_3 (containing only surface Lewis acid sites). The plots of band intensities versus the concentration of molecules adsorbed were linear, and the values of extinction coefficients were calculated from the slopes of the lines. Following values have been obtained: 0.070 cm/μmol (PyH^+), 0.11 cm/μmol (NH_4^+), 0.100 cm/μmol (PyL) and 0.026 cm/μmol (NH_3L). The concentration of Brønsted and Lewis acid sites determined with pyridine and ammonia on Al_2O_3, on aluminosilicates, and in HMCM-41 (Si/Al = 10) are presented in Table 1.

Generally, the concentrations of acid sites of Brønsted and Lewis type determined with pyridine are distinctly lower than those determined with ammonia. It should be noted, that in the case of zeolites the concentration of acid sites determined with pyridine and ammonia were the same [27]. It is not excluded, that despite of the presence of large pores in our mesoporous materials, some acid sites may be situated inside very narrow pores or very small cages being inaccessible to bulky pyridine molecules but accessible to ammonia.

The concentration of Brønsted acid sites increases with Si content due to the formation of acidic Si–OH–Al, and at high Si/Al it increases also due to the growing surface area (see Table 1). The concentration of Brønsted acid sites expressed per 1 m^2 of surface area increases with Si/Al until Si/Al = 2, and next, at higher Si/Al, decreases due to the 'dilution' of acid sites with Si species not having neighboring Al, and therefore not able to form Si–OH–Al. The concentration of Lewis sites decreases with Si content due to the transformation of surface Al species which are potential Lewis sites into Si–OH–Al and also to dilution of the material with Si species.

The sum of the concentrations of Brønsted and Lewis acid sites divided by the amount of Al in Al_2O_3 and aluminosilicates (B + L)/Al expressing which fraction of Al atoms is able to form either Brønsted or Lewis acid sites (in both of them Al is engaged) is also presented in Table 1. In mesoporous Al_2O_3 itself only 5% of all Al atoms is able to be Lewis acid sites, the rest is either hidden in the bulk, or on the surface, but the coordination of Al with oxygen atoms excludes the possibility of coordination of electrondonor molecules such as NH_3. The (B + L)/Al values increase with Si content. This may be due to two reasons: at high Si/Al (Si/Al > 2) the surface area increase and therefore more Al atoms is exposed to the surface and may participate in the formation of acid sites. However, if Si/Al ≤ 2 the surface area is practically constant, but (B + L)/Al values do increase from 0.05 to 0.15. This may be due to the fact, that some Al atoms which were not engaged into the formation of acid sites became involved into the creation of Brønsted sites (Si–OH–Al moieties) if Si content increases.

The information on the acid strength of both Lewis and Brønsted sites was obtained in the experiments of ammonia and pyridine desorption. The excess of pyridine, or ammonia was adsorbed at 440 and 370 K, respectively, and next physisorbed molecules have been removed by the evacuation at the same temperature as adsorption was performed. The adsorbed bases were subsequently desorbed at 570 (pyridine) or 500 K (ammonia), and the ratios $A_{des.}/A_0$ (where A_0 and $A_{des.}$ are the intensities of IR bands of ammonia or pyridine bonded to both Brønsted and Lewis sites upon the evacuation at 420 K and upon the desorption, respectively) were taken as the measure of the acid strength of both Lewis and Brønsted acid sites. These values are presented in Table 1.

The acid strength of Lewis sites (both measured by pyridine and ammonia) increases with the Si content, what agrees with the results of CO adsorption (Fig. 1), which evidenced the increase of the contribution of strong Lewis sites (CO band 2225 cm^{-1}) produced by dehydroxylation and with the data presented in Fig. 5 (higher frequency of the band of PyL species). The acid strength of Brønsted sites does not show any reasonable dependence on the content of Si incorporated, suggesting that all the Brønsted acid sites produced by the Si insertion have similar acid strength.

3.3. Comparison of acid properties of aluminosilicates of the same Si/Al (Si/Al = 10) but synthesized by different methods

As our SA material of high silicon content has hexagonal arrangement of pores similar to typical MCM-41, it was interesting to compare how the differences of synthesis conditions influence on the acid properties of these

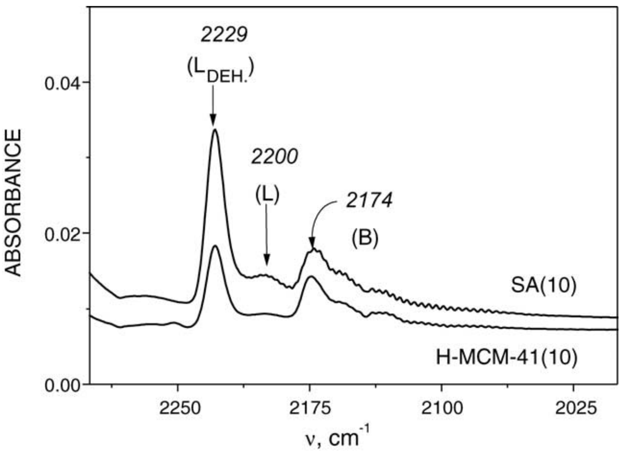

Fig. 8. IR spectra of CO adsorbed at 170 K on SA (10) and on HMCM-41.

materials. Two different synthesis methods were applied for the preparation of mesoporous aluminosilicates of similar chemical composition. We assumed that different synthesis conditions such as: different temperature, chemicals used, and synthesis procedure could influence on extent of Al incorporation and/or its distribution within mesoporous structure which could affect the acidity.

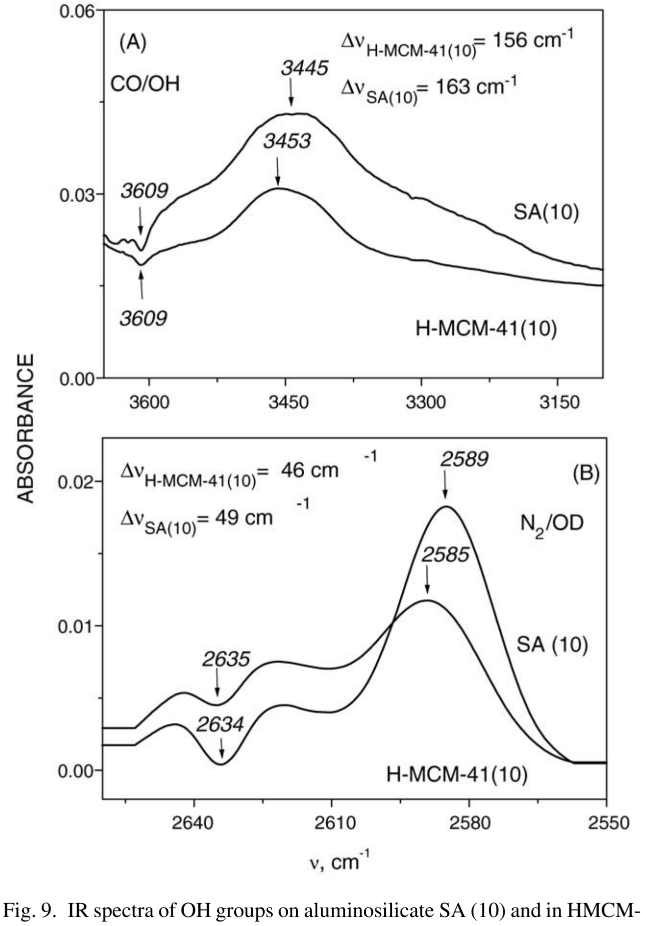

Fig. 9. IR spectra of OH groups on aluminosilicate SA (10) and in HMCM-41 interacting with CO (A), as well as OD groups in deuterated materials interacting with N_2 (B).

The spectrum of OH groups in HMCM-41 is presented in Fig. 8 together with the spectrum of SA (10). Similarly as in the case of SA (10) the spectrum of HMCM-41 shows the band of Si–OH–Al groups at 3605 cm^{-1}. The Si–OD–Al band at 2633 cm^{-1} is also present in the spectrum of deuterated sample.

The concentration of acid sites in SA (10) and HMCM-41 is presented in Table 1. The concentration of both Brønsted and Lewis sites is higher in the case of SA. Similarly, the value (B + L)/Al is higher for SA (10). All these results indicate that the synthesis method applied in this work for SA formation (via atrane complexes) is more efficient way to generate acid sites of both Lewis and Brønsted (Si–OH–Al) type. Maybe the synthesis of SA via atrane complexes leads to more homogenous Al distribution and its preferential localization on mesopores walls (better accessibility to probe molecules and reactants).

The experiments with pyridine and ammonia desorption evidenced that the acid strength of Lewis sites in SA was higher than in HMCM-41. This can be related to higher contribution of strong Lewis sites produced by dehydroxylation of Si–OH–Al seen in the spectra of adsorbed CO (higher intensity of 2229 cm^{-1} band in SA—Fig. 8).

The information on the strength of Brønsted acid sites was obtained in the experiments of pyridine and ammonia desorption as well as by comparing of the values of frequency shifts $\Delta\nu$ of IR bands of OH interacting with CO and OD interacting with N_2 (Fig. 9). All the data lead to the conclusion that the acid strength of Brønsted sites is higher in SA (10), than in HMCM-41 of the same Si/Al. This is evidenced by higher $A_{des.}/A_0$ and higher $\Delta\nu$ values.

Therefore the mesoporous aluminosilicates produced on the basis of alumina show not only higher concentration of acid sites but also higher strength of acid sites than mesoporous HMCM-41. They may be effective acid catalysts for reactions for bulky reactant molecules.

Acknowledgements

This study was sponsored by the Polish Ministry of Scientific Research and Information Technology (grant no. 4 T09A 184 24) and by NATO 'Science for Peace' program (grant NATO SfP no. 974217). PS acknowledges support from ESF grant no. 5936.

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