UNIFORMITY AND ORDERING OF INNER WALLS OF (Al)MCM-41

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The uniformity and ordering of the surface of (Al)MCM-41 channel walls was investigated employing bare Co(II) ions as probes. VIS spectra of Co(II) ions evidenced the presence of two types of uniform cationic sites in dehydrated Co-(Al)MCM-41 in a wide range of Si/Al/Co chemical composition (Si/Al = 11–76, Co/Al = 0.08–0.44). These cationic sites represent centers of two types of uniform domains, containing in minimum 18 surface T atoms, present on the surface of the channel walls of (Al)MCM-41. These domains represent majority of the inner surface of the (Al)MCM-41 molecular sieve.
Keywords: Mesoporous materials; Molecular sieves; (Al)MCM-41; VIS spectroscopy; Co(II) ions; Heterogeneous catalysis.

The discovery of mesoporous molecular sieves of the M41S family[1], and the possibility to introduce other elements (Al, Fe) into the siliceous mesoporous molecular sieves[2,3], opened new possibilities for the preparation of catalysts with tunable size of uniform pores in the mesoporous range, easily accessible for bulky molecules and with tunable Si/Al chemical composition.

In contrast to the microporous molecular sieves, no information on the local arrangement and on the regularity and uniformity of the surface of the mesoporous molecular sieve channels is available. Combination of the diffraction and adsorption techniques and electron microscopy enables only to identify the mesoporous molecular sieve ordering, space group symmetry, surface area, channel size and channel wall thickness. However, catalytic properties of active sites depend on their local arrangement, *i.e.* on the local framework topology, framework negative charge density and on the uniformity of active sites.

The surface of mesoporous molecular sieves is usually regarded as amorphous and simple models present the channel surface of MCM-41 being formed from regular six-member rings[4]. However, there is no experimental

evidence for this assumption. Thus, the information on the local structure and/or ordering of MCM-41 is highly demanded, mainly for application of mesoporous molecular sieves in acid and base catalysis.

Recently, we have successfully employed VIS spectroscopy of bare Co(II) ions for the description of cationic sites in silicon rich pentasil zeolites[5–10] and for the investigation of Al distribution in (Al)MCM-41 (ref.[11]). According to these studies, Co(II) ions followed by VIS spectroscopy were found to be an excellent probe for the investigation of silicon rich molecular sieves. In this paper, an attempt is made to elucidate the uniformity and ordering of the surface of (Al)MCM-41 channel walls employing bare Co(II) ions as probes.

EXPERIMENTAL

Synthesis and Characterization of (Al)MCM-41

(Al)MCM-41 with Si/Al ratio in the range 11–76 were synthesized from sodium silicate, hexadecyltrimethylammonium bromide, ethyl acetate and aluminium hydroxide modifying the procedure described in refs[11–13].

Structure and properties of calcined and ion exchanged (Al)MCM-41 (see later) were checked using X-ray powder diffraction, adsorption of nitrogen, FTIR spectroscopy and ^{27}Al MAS NMR. Powder XRD patterns of (Al)MCM-41 were collected using diffractometer Siemens D5005 in the Bragg–Brentano geometry arrangement with CuKα radiation. Adsorption isotherms of nitrogen were recorded at 77 K with an Accusorb 2100E instrument (Micromeritics). The samples were activated for about 20 h at 350 °C at the pressure of 10^{-4} Pa before the measurement. FTIR spectra of dehydrated (Al)MCM-41 in the region of OH stretching vibrations were recorded using self-supported wafers of thickness *ca* 10 mg cm^{-2} on FTIR spectrometer Nicolet Magna-550 with KBr detector and a cell with CaF$_2$ windows connected to vacuum apparatus. ^{27}Al MAS NMR spectra of hydrated (Al)MCM-41 were measured on a Bruker AMX500 spectrometer using home-made probe heads with 3.5 mm o.d. rotors. For details on XRD diffraction, nitrogen adsorption and FTIR see refs[11,14].

All Co-(Al)MCM-41 represented well ordered mesoporous materials and exhibited adsorption characteristics typical for mesoporous materials with small pore size distribution. ^{27}Al MAS NMR and FTIR spectra excluded the presence of significant concentration of octahedrally coordinated Al in the samples.

Ion Exchange of (Al)MCM-41

Co^{2+} ions were incorporated into calcined (Al)MCM-41 *via* ion exchange performed using cobalt (II) nitrate solution at ambient temperature. Chemical composition of Co exchanged (Al)MCM-41 samples was estimated after their dissolution by chelatometric titration (Al), gravimetry (Si) and atomic absorption spectrometry (Co) and is given together with details on sample preparation in the Table I. After ion-exchange the individual samples were carefully washed by distilled water, dried at ambient temperature and grained.

UV-VIS-NIR Diffuse Reflectance Spectroscopy

Prior to the spectra monitoring, the Co^{2+} samples were dehydrated at 750 K under vacuum of $7 \cdot 10^{-2}$ Pa for 3 h. Dehydration was carried out with a heating rate of 5 K min^{-1}. After dehydration, the sample was cooled down to ambient temperature and transferred under vacuum into the optical cell and sealed. UV-VIS-NIR diffuse reflectance spectra (4 000–50 000 cm^{-1}) were recorded using a Perkin–Elmer UV-VIS-NIR spectrometer Lambda 19 equipped with a diffuse reflectance attachment with an integrating sphere coated by $BaSO_4$. Spectra of sample in 5 mm thick silica cell were recorded in a differential mode with the parent zeolite treated at the same conditions as a reference. For details see refs[5–7]. The absorption intensity was calculated from the Schuster–Kubelka–Munk equation $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the diffuse reflectance of a semi-infinite layer and $F(R_\infty)$ is proportional to the absorption coefficient.

RESULTS

The absence of the combination vibration bands of water (5 260 and 7 120 cm^{-1}) in the NIR spectrum (not shown in figures) of dehydrated Co-(Al)MCM-41 reflects complete dehydration of the Co^{2+} molecular sieves. The presence of only one combination vibration band corresponding to Si–Al–OH bridging groups (7 320 cm^{-1}) in the NIR spectrum of Co-(Al)MCM-41 indicates that Co–OH group was not formed during dehydration. For details on NIR spectra of dehydrated Co(II) molecular sieves *cf.* refs[5–7,10,11,14]. Thus, it can be concluded that UV-VIS-NIR spectra evidenced the exclusive presence of bare Co(II) ions in dehydrated Co-(Al)MCM-41.

TABLE I
Chemical composition of Co-(Al)MCM-41 and conditions of their preparation

Molecular sieve	Si/Al	Co/Al	Co concentration in solution mol l^{-1}	Volume of solution per 1 g of zeolite ml g^{-1}	Time of exchange h
Co-(Al)MCM-41	11	0.17	0.05	$3 \cdot 140^a$	$3 \cdot 24^a$
Co-(Al)MCM-41	19	0.26	0.05	$3 \cdot 140^a$	$3 \cdot 24^a$
Co-(Al)MCM-41	42.5	0.08	0.05	6	12
Co-(Al)MCM-41	42.5	0.11	0.05	20	12
Co-(Al)MCM-41	42.5	0.26	0.05	$2 \cdot 140^b$	$3 \cdot 12^b$
Co-(Al)MCM-41	76	0.44	0.05	$3 \cdot 140^a$	$3 \cdot 24^a$

^{a} Three step ion exchange; ^{b} two step ion exchange.

The VIS spectra of Co(II) ions in dehydrated Co-(Al)MCM-41 depends both on the Co loading in the molecular sieve and on their framework Al content, as follows from Fig. 1, where normalized VIS spectra of dehydrated Co-(Al)MCM-41 are given. This indicates the presence of several Co(II) coordinations in dehydrated molecular sieves, *i.e.* the presence of several cationic sites for divalent cations. To identify the spectra corresponding to the individual Co^{2+} sites, second derivative mode analysis (not shown here) and decomposition of the spectra to the Gaussian curves were used (for details see refs[5–7]). Decomposition of the VIS absorption of the Co-(Al)MCM-41 to the Gaussian curves evidences the presence of two types of Co(II) ions, as it is illustrated in Fig. 2. Co-1 ions are reflected in the VIS spectrum by a single band with maximum at 14 600 cm^{-1}. These Co(II) ions are preferentially present at high Co loadings in the molecular sieve or in (Al)MCM-41 with low framework Al content. Co-2 ions correspond to the spectrum composed from four bands at 15 850, 17 450, 19 970 and 21 700 cm^{-1}. These Co(II) ions predominate in the Co-(Al)MCM-41 with low Co loading or with high framework Al content. Positions of the Co(II) bands together with their width are summarized in Table II and compared with Co(II) observed in pentasil ring zeolites.
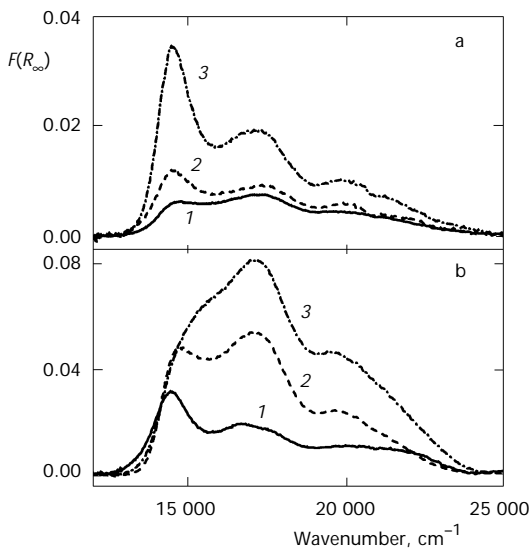

FIG. 1
Effect of a Co loading on VIS spectra of dehydrated Co-(Al)MCM-41 (Si/Al = 42.5, Co/Al = 0.08 (*1*), 0.11 (*2*) and 0.26 (*3*)) and b framework Al content on VIS spectra of dehydrated Co-(Al)MCM-41 with maximum Co loading (Si/Al = 76 (*1*), 19 (*2*) and 11 (*3*))

DISCUSSION

Because the d–d transitions of the Co(II) ions, reflected in VIS spectrum, are sensitive to the ion local environment, VIS spectra of bare Co(II) ions can been used as fingerprints of Co(II) ion cationic sites in zeolites, for details see refs[5–7]. Based on this approach, two types of bare Co(II) ions are formed in Co-(Al)MCM-41, *cf.* also refs[11,14]. As follows from Table II, the VIS spectra of Co-1 and Co-2 ions are similar to the spectra of Co(II) ions of the type α and β in pentasil ring zeolites of mordenite, ferrierite and ZSM-5 structure.

TABLE II
Spectra of bare Co(II) ions in Co-(Al)MCM-41 (Co-1,2) and in pentasil ring zeolites (Co-α,β,γ)

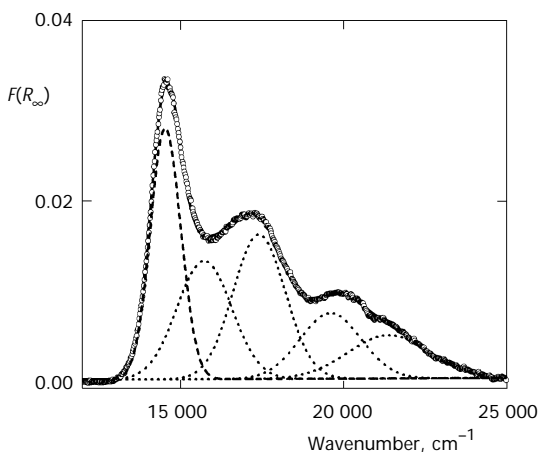| Matrix	Co(II) bands, cm^{-1}							Band width, cm^{-1}		
	Co-1/α	Co-2/β				γ		Co-1/α	Co-2/β	γ
MCM-41	14 500	15 900	17 300	19 700	21 500			1 200	2 200	
MOR	14 800	15 900	17 500	19 200	21 100	20 150	22 050	1 200	2 100	1 300
FER	15 000	16 000	17 100	18 700	20 600	20 300	22 000	1 100	1 900	1 200
ZSM-5	15 100	16 000	17 150	18 600	21 200	20 100	22 000	1 800	2 100	1 400

FIG. 2
Decomposition of the VIS spectrum of dehydrated Co-(Al)MCM-41 (Si/Al = 42.5, Co/Al = 0.26) to the Gaussian bands. Experimental data (○), fit (–––––), Gaussian bands corresponding to Co-1 (– – –) and Co-2 (· · · ·) Co(II) ions

Each type of bare Co(II) ion observed for pentasil ring zeolites was attributed to the specific cationic site in these zeolites[5–7]. Thus, the presence of Co-1 and Co-2 ions in dehydrated Co-(Al)MCM-41 evidences the presence of two types of cationic sites for divalent cations in (Al)MCM-41, Co-2 site represent majority of Co(II) sites in (Al)MCM-41. As follows from Table II, band width of absorption bands of bare Co(II) in (Al)MCM-41 is comparable with that of Co(II) ions in zeolites. This indicated that cation siting in (Al)MCM-41 is uniform in the sense of the uniformity of cation siting in silicon rich zeolites. This suggestion is further supported by the fact, that while the concentration of the individual types of the Co(II) ion in Co-(Al)MCM-41 depends on Co/Si/Al ratio, positions of absorption bands are independent on the chemical composition in a wide range (Si/Al = 11–76, Co/Al = 0.08–0.44).

Similarity of the spectra of Co-1 and Co-2 ions in (Al)MCM-41 and Co-α and Co-β in pentasil ring zeolites indicates similarity of the cationic sites. However, on contrary to zeolites, framework structure of MCM-41 is not known. Thus, the identification of the geometry of cationic sites cannot be made on the parallel between the spectra of the Co(II) ions in various matrices and local framework arrangement of these matrices and requires further studies.

The coordination of the Co(II) ion to the cationic site is followed by the deformation of the site geometry. This local perturbation of the framework is reflected in the shift of skeletal antisymmetric T–O–T vibrations[10,15]. However, despite this rearrangement of the geometry of cationic site, Co(II) spectra reflect small differences in the geometry of similar sites in different zeolites, *cf.* Table II and refs[5–7,10,11,14]. Thus, small differences both in the local geometry and deformability of cationic sites are reflected in the spectrum of bare Co(II) ions. No changes in the Co-1 and Co-2 spectra were observed for Co(II)-(Al)MCM-41. Thus, the local arrangement of two types of Co(II) ion sites in (Al)MCM-41 is uniform in the sense of uniformity of cationic sites in zeolites.

Note that this local arrangement does not represent only the ring accommodating Co(II) ion. Uniformity of larger area is necessary to guarantee the formation of uniform Co(II)-ring structure. Thus, the nearest neighbors of the T atoms forming six-member rings (minimum size of ring accommodating cation in pentasil ring zeolites) at least and their next-nearest neighbors with high probability can be supposed to be uniformly arranged in the sense of the uniformity of the zeolite framework. It indicates that on the surface of the (Al)MCM-41 channels two types of uniform domains are present, consisting of two types of rings in their centers. These domains are

composed from *ca* 18 to 24 surface T atoms, depending if the central rings are surrounded by six-member or five-member rings or by their combination.

Maximum obtained Co/Al ratio reached 0.17 for Co-(Al)MCM-41 with Si/Al = 11. However, only 56% of Al atoms are present in the (Al)MCM-41 channel surface (see ref.[14]), the rest of Al atoms is present in the inner layers of the channel walls. Moreover, the surface layer of the channel wall contains only 30–40% of all T atoms due to the usual wall thickness of samples in the range of 10–15 Å (wall thickness according XRD and adsorption isotherm for nitrogen, for details see ref.[11]). Thus, the Si/Al ratio of the surface layer of the (Al)MCM-41 (Si/Al = 1.1) channel wall is 6–8 and surface Co/Al ratio 0.3. From this chemical composition of the channel surface follows that to one Co(II) ion, *i.e.* to one uniform domain (18–24 T atoms) correspond 23–37 surface T atoms. Thus, 50–95% of the surface T atoms form uniform domains of nearest and next-nearest neighbors. Even in the case of the smallest thinkable domains containing only nearest neighbors (*i.e.* 12 T atoms), these domains represent 30–50% of surface T atoms. This indicates that dominant part of the surface of (Al)MCM-41 channel walls is formed by two types of uniform domains.

In conclusion, the majority of the surface of the (Al)MCM-41 channels is composed from two types of domains. These domains containing *ca* 18–24 surface T atoms are uniform and form cationic sites for divalent cation. Domains containing Co-2 cationic sites represent majority of cationic sites and, thus, majority of ordered (Al)MCM-41 channel surface.

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