

Al distribution in ZSM-5 zeolites: an experimental study

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Received (in Cambridge, UK) 29th November 2000, Accepted 19th April 2001

First published as an Advance Article on the web 10th May 2001

Al atoms are not randomly distributed in ZSM-5 zeolites but their distribution is affected by the Si/Al composition and the synthesis procedure.

Zeolites with low concentration of aluminium in the framework ($\text{Si/Al} > 8$), such as *e.g.* those with the ZSM-5 structure, constitute a basis for catalysts of high significance in both acid-base and redox catalysis. Because of the low aluminium content, local Si–Al sequences described as ‘Al pairs’ [$\text{Al–O–(Si–O)}_{1,2}\text{–Al}$] and ‘single’ Al atoms [$\text{Al–O–(Si–O)}_{\geq 3}\text{–Al}$] that are far apart, are present in their frameworks.¹ Therefore, with divalent cations complete ion exchange is not possible.² Spatial distribution of the Si–Al sequences also leads to variations in the aluminium distribution in the zeolite channel system. As the occurrence and distribution of Al in the zeolite framework controls the presence, distribution and properties of catalytically active sites, *i.e.* of protonic and metal ion sites, the distribution of aluminium in the framework is very important for the catalytic properties of these materials. The presence of Al pairs is necessary for the exchange of divalent cations,³ and the geometry of zeolite rings accommodating Al pairs affects coordination of the cations in zeolites.³ However, no method is available for determination of the distribution of Al in silicon-rich zeolites. ²⁹Si MAS NMR can distinguish only Al–O–Si–O–Al pairs (representing only a minority of the Al pairs, <5% Al, in ZSM-5⁴), while Al–O–(Si–O)₂–Al sequences cannot be distinguished from single Al atoms. Also ²⁷Al MAS NMR spectroscopy cannot provide such information. The theoretical approach using Monte Carlo simulation, based on the premise that Al distribution in zeolites is random, or quantum chemical studies modeling small clusters thus face severe limitations. Moreover, they cannot reflect the potential dynamic effect occurring during zeolite synthesis.

We suggest an indirect method for the estimation of the number of Al pairs and single Al atoms present in zeolites and of the distribution of Al pairs in framework local structures (cationic sites) in the zeolite channels. The method is based on monitoring of the distribution of bare divalent Co(II) ions, coordinated exclusively to framework oxygen atoms, at the cationic sites of dehydrated Co-zeolites exchanged to the maximum degree. To balance the positive charge of these bare divalent cations, two negative AlO_2^- charges are required at the cationic site. The d–d transitions of bare Co(II) ions in the Vis region reflect their coordination at the local geometry of the framework cationic sites. Three different cationic sites denoted as α , β and γ were suggested for bare Co(II) ions in mordenite, ferrierite and ZSM-5 structures.^{5–7} In the case of the ZSM-5 matrix, Co(II) ions in the α site, characterized by a single band at $15\,100\text{ cm}^{-1}$, represent the Co(II) ions located above four framework oxygens forming a plane in the deformed six-membered ring composed of two five-membered rings. The Co(II) ions in the β site are located in another type of deformed six-membered ring, and their spectrum is composed of four bands at $16\,000$, $17\,150$, $18\,600$ and $21\,200\text{ cm}^{-1}$. The Co(II) ions in the ‘boat shaped’ γ site lead to a doublet of bands at $20\,100$ and $22\,000\text{ cm}^{-1}$. A schematic representation of these cationic sites is given in Fig. 1, (for details see ref. 7). Quantitative analysis of the corresponding Co(II) spectra provided the concentration and distribution of the Co(II) ions in

the individual cationic sites of pentasil ring zeolites. Because bare Co(II) ions must be balanced by two framework AlO_2^- tetrahedra, the distribution of the bare Co(II) ions among the cationic sites in Co-ZSM-5 with maximum loading of the exchanged bare Co ions reflects the distribution of Al pairs [$\text{Al–O–(Si–O)}_{1,2}\text{–Al}$] at different cationic sites. Therefore, the bare Co(II) ions with characteristic spectral features can serve as probes for the distribution of Al pairs in zeolites.

To guarantee that the monitored Co(II) ions are counter ions to Al pairs, they should be present in the form of bare cations bound only to framework oxygens without coordinating extraframework ligands. This was confirmed by the NIR–Vis–UV spectra of dehydrated Co-ZSM-5 and supported by FTIR and EXAFS results. The absence of Co(II) ions coordinated to weak extraframework ligands, such as water or OH groups, was evidenced by the absence of the combination vibration bands around 5200 cm^{-1} (water) and 7200 cm^{-1} (water and OH). Also the band at $3650\text{–}3660\text{ cm}^{-1}$, which reflects OH groups bound to Co or extraframework Al, was not found in the IR spectra of Co-ZSM-5 as well as in those of parent Na-ZSM-5. The latter information together with the ²⁷Al MAS NMR of Na-ZSM-5, indicating only T_d coordinated aluminium, evidenced that all aluminium was present in the zeolite frameworks. Coordination of the Co(II) ion to strong ligands such as an extraframework oxygen atom (Co–O–Co species) lead to intense charge transfer bands, which, however, are not found in the UV spectral region. Moreover, EXAFS results on Co-ZSM-5/A (Si/Al 14.1) showed Co(II) ions coordinated only to framework oxygens, and Co–O–Co type bonding was not detected.⁸ Thus, the NIR–Vis–UV spectra can be used to provide evidence for the dominant presence of bare Co(II) ions in dehydrated Co-zeolites and for the estimation of the concentration and distribution of the Co(II) ions at the cationic sites.

The concentration of Al pairs in ZSM-5/A and B series† was obtained from the above described quantitative analysis of the Co(II) VIS spectra of Co-ZSM-5 zeolites with maximum loading of bare Co(II) ions (see ref. 7 and above). The effect of the procedure of zeolite synthesis and of the framework aluminium content in the ZSM-5 matrix (expressed as Si/Al ratio) on the relative concentration of Al pairs in α , β and γ sites (derived from absolute concentrations) is depicted in Fig. 2. The sum of the concentrations of Al pairs in α , β and γ sites

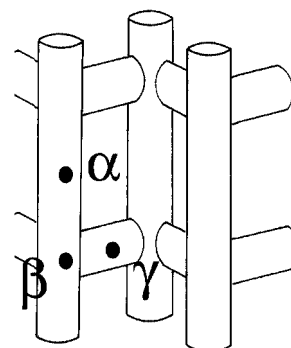


Fig. 1 Position of α , β and γ sites of the Co(II) ions in ZSM-5.

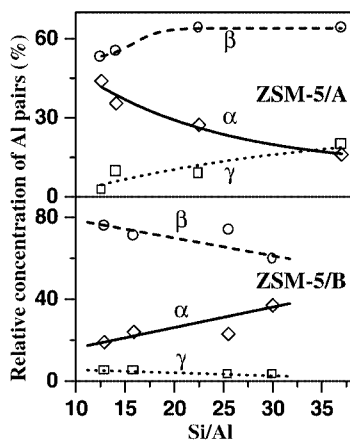


Fig. 2 Effect of Si/Al on relative concentration of Al pairs in α (—), β (---) and γ (····) sites for ZSM-5/A and /B.

represents the total concentration of Al pairs in the zeolite framework. The concentration of single Al atoms can be obtained as a difference between the total framework Al concentration (from bulk analysis, note that the extraframework Al species were not detected) and the concentration of Al pairs. The effect of the procedure of zeolite synthesis and of the framework aluminium content on the relative concentration of Al pairs and single Al atoms is described in Fig. 3. It is evident that the total concentration of Al pairs and single Al atoms as well as the relative concentration of Al pairs at the α , β and γ

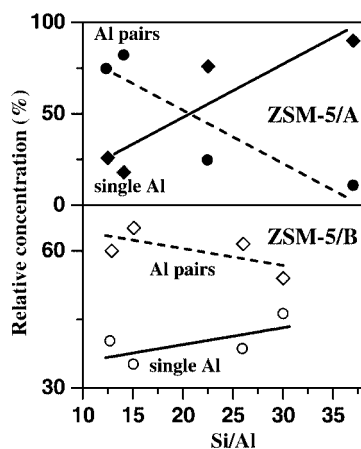


Fig. 3 Effect of Si/Al on relative concentration of single Al atoms (—) and Al pairs (---) for ZSM-5/A and /B.

cationic sites depend dramatically on the Si/Al composition and on the synthesis procedure.

The assumption of random or statistically controlled distribution of aluminium¹ cannot explain the dramatic differences in the Al distribution in zeolites synthesized under different conditions, and the dependence of the relative concentration of Al pairs in the α , β and γ sites on the Si/Al ratio. The results imply that the aluminium distribution in ZSM-5 is not random and not controlled exclusively by statistical rules. Preferences for the formation of single Al atoms and Al pairs in specific framework local structures play a significant role during zeolite synthesis and depend on the synthesis conditions.

It can be concluded that the Al distribution in silicon-rich molecular sieves is not random, but depends on the chemical composition of the zeolite and on the conditions of synthesis. The bare Co(II) ions detected by Vis spectroscopy represent a powerful tool for investigation of the Al distribution in silicon-rich zeolites. This provides a potential (i) for investigation of the relation between the activity of catalysts based on silicon-rich zeolites and the aluminium distribution in their framework, and (ii) for controlling the Al distribution in the framework of these zeolites by variation of synthesis procedures.

Financial support by the Grant Agency of the Czech Republic under the project # 104/00/0640 and by the EC COST program, project # D15/0014/00-OC D15.20 is gratefully acknowledged.

Notes and references

† ZSM-5 zeolites were prepared by two types of synthesis procedure. ZSM-5/A (Si/Al 12.5, 14.1, 22.5, 37) was provided by Slovnaft, Slovakia and ZSM-5/B (Si/Al 12.9, 15.9, 25.5, 30) was provided by the Research Institute of Inorganic Chemistry, Inc., Czech Republic. The parent Na-zeolites were ion-exchanged three times with 0.1 M Co(NO₃)₂ at ambient temperature. Dehydration of the samples was conducted at 770 K for 3 h under a dynamic vacuum up to 10⁻⁵ Torr.

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