Control of Al distribution in ZSM-5 by conditions of zeolite synthesis

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Concentration of Al–O–(Si–O)$_{1,2}$–Al sequences located in one ring and forming cationic sites for divalent cations in ZSM-5 can be controlled in a wide range of their concentrations by the variation of the source of aluminium and silicon used for synthesis of this zeolite.

Silicon-rich zeolites have attracted considerable attention due their chemical and structural properties to be used in catalysis, adsorption and separation. The understanding of the properties and behaviour of these molecular sieves is rather limited, as there is a lack of the knowledge on the location and distribution of aluminium in the silicate framework and on the relationship between aluminium siting and distribution and the behaviour of these materials. This is caused by the fact that there does not exist any experimental technique to directly determine the location of the aluminium in the framework. Aluminium distribution in the zeolite framework can be regarded from various points of view, beside them the formation of various Al–O–(Si–O)$_x$–Al sequences and their locations in the channel system is of extremely high importance. In principle, aluminium atoms can be located in the framework of silicon-rich zeolites as "single" Al atoms [(Si–O)$_{n>2}$–Al–O–(Si–O)$_{n>2}$ sequences] which are unable to be balanced by cobalt(II) hexaaqua-complexes in hydrated zeolites; "close unpaired" Al atoms [(Si–O)$_{n>2}$–Al–O–(Si–O)$_{n>2}$ sequences] close enough to accommodate cobalt(II) hexaaqua-complexes in hydrated zeolite, but not forming cationic sites for "bare" divalent cations (without extra-framework ligands) in dehydrated zeolites and Al "pairs" [Al–O–(Si–O)$_{1,2}$–Al sequences] located in one ring forming cationic sites for "bare" divalent cations.[1,2] Note, that the ion-exchange capacity of divalent metal cations depends on their size.[3] It is clear that the knowledge of the location and distribution of such Al–O–(Si–O)$_x$–Al sequences in zeolites is decisive for their application in redox catalysis.[4] No direct evidence has been provided that the distribution of Al atoms into "single" Al atoms and Al "pairs" controls the rate of acid catalysed reactions. However, it is assumed that certain elementary steps in the reaction pathways may be favoured if two acid sites are close to each other instead of being isolated.[5] The lack of the knowledge in this area is probably connected with the fact that detailed descriptions of Al distribution are still missing and zeolites with controlled Al distribution are not available.

Recently, Sastre *et al.* have proposed the possible Al and proton siting in zeolite ITQ-7, combining force field atomistic simulations and FTIR experiments.[6] They assumed that Al distribution is controlled by the energetics during the synthesis process and the interaction between the structure-directing agent and the zeolite framework has to be involved in the model. Based on this assumption, variation of the structure-directing agent can be employed to control the distribution of framework negative charge in zeolites.

In our previous papers, we have suggested that the distribution of Al in silicon-rich zeolites among "single" Al atoms, "close unpaired" Al atoms and Al "pairs" can be estimated by using the UV-Vis spectra of Co(II) ions in dehydrated zeolites at maximum Co(II) loading.[1,2] Moreover, it was demonstrated that Al distribution in ZSM-5 is not controlled by statistic rules and

depends on the conditions of the zeolite synthesis. It should be stressed that the results concerning the number of "close unpaired" Al atoms and "single" Al atoms are influenced by the size of Co(II) ions and different quantitative data could be obtained using divalent cations of significantly different size. However, this fact will not affect the conclusions drawn for the effect of the synthesis conditions on the aluminium distribution. Although some rare information can be derived on aluminium distribution from above mentioned papers, no attempt appeared up to now to control the Al distribution *via* the synthesis procedure. In this contribution, we tried to control the Al distribution among "single" Al atoms and "close unpaired" Al atoms and Al "pairs" *via* carefully performed synthesis and to elucidate the effect of silica and aluminium sources on the distribution of Al atoms in ZSM-5 zeolite.

A series of ZSM-5 zeolites, with Si/Al ranging from 23 to 38, differing in the source of aluminium and silicon were prepared under hydrothermal conditions. All syntheses were carried out under autogeneous pressure at 170 °C with agitation for 7 to 10 days depending on the source of aluminium. The synthesis procedure of zeolite ZSM-5 (Si/Al = 25) using Al(NO$_3$)$_3$·9H$_2$O (Fluka, 98 %) as the Al source and TEOS (tetraethoxy orthosilicate, Aldrich, 98%) as the Si source was as follows: 1.65 g Al(NO$_3$)$_3$·9H$_2$O was dissolved in 10 ml of distilled water. 22.6 g Of TEOS and 5 ml of ethanol were slowly added under stirring. The solution was stirred for 90 min. In another beaker 40.75 g of TPAOH (tetrapropylammonium hydroxide, 20% solution in water, Fluka) was blended with 40 ml of distilled water and stirred for 90 min. After that the solution of TPAOH was added to the initial solution of precursors. Finally the mixture was stirred for another 90 min and the homogenous solution was put into an Teflon-lined autoclave (volume 90 ml). The composition of the initial gel with Si/Al = 25 was the following: Al$_2$O$_3$: SiO$_2$: EtOH : TPAOH : H$_2$O = 1 : 50 : 79 : 18 : 2091. The synthesis procedure was varied by using different aluminium and/or silica sources: (Al(NO$_3$)$_3$·9H$_2$O, aluminium hydroxide (Fluka, 64–66% Al$_2$O$_3$), AlCl$_3$·6H$_2$O (Fluka, 99%), aluminium-tri-*sec*-butoxide (Aldrich, 98%), Cab–O–Sil M5 (Cabot GmbH), Ludox LS-30 (Aldrich, 30 wt% SiO$_2$ in aqueous solution) and sodium silicate (Riedel-deHaën, 27% SiO$_2$, 10% NaOH). All zeolites synthesised were calcined in a stream of air at 500 °C for 8 hours. Calcined samples were ion exchanged with 0.5 M solution of NaCl to obtain Na-ZSM-5. Maximum loaded co-zeolites were prepared by three times repeated ion exchange of Na-zeolites with 0.05 M solution of Co(NO$_3$)$_2$ at ambient temperature. The chemical composition of the Na- and Co-samples was estimated after their dissolution by atomic absorption spectroscopy.

XRD, KBr-FTIR and SEM indicated good crystallinity of the calcined samples. The charge balance of sodium exchanged samples and the FTIR study of acid sites indicated only a negligible amount of extraframework Al, see ref. 2. The ion exchange capacity of zeolites for Co(II) hexaaqua-complexes combined with UV-Vis diffuse reflectance spectroscopy (DRS) of hydrated and dehydrated Co-zeolites were used for the determination of Al distribution. Prior to the spectra measurement, samples were dehydrated for 3 hours at 450 °C in a vacuum. Spectra were recorded using a Lambda 19 Perkin-

Elmer UV-Vis-NIR spectrometer equipped with a diffuse reflectance attachment with an integrating sphere coated by $BaSO_4$, and $BaSO_4$ as a standard, see ref. 7

As follows from the ion exchange capacity of ZSM-5 zeolites for Co(II) hexaaqua-complexes and from the visible spectra of dehydrated Co-zeolites (not shown), samples with similar aluminium content, but differing in the aluminium distribution, were prepared using different aluminium and silicon sources. It indicates that the nature of aluminium and silicon sources and the related formation of complex poly-oxo-anions containing Si and Al in the synthesis gel dramatically affect aluminium distribution in silicon rich zeolites and thus, zeolite properties are influenced by this distribution.

In the case of TEOS as the silica source, zeolites with a similar distribution of single and close Al atoms were obtained using $Al(NO_3)_3$ and Al-*sec*-butoxide. "Single" aluminium atoms represented the majority of Al atoms ($> 90\%$). No "close unpaired" Al atoms were observed. The use of $AlCl_3$ or $Al(OH)_3$ resulted in a significant increase in the amount of Al–O–(Si–O)$_{1,2}$–Al sequences located in one ring (33 and 27% using $AlCl_3$, $Al(OH)_3$, respectively). Moreover, close unpaired Al atoms (3%) were present in the ZSM-5 zeolite prepared using $AlCl_3$. The rest of the Al atoms (*ca.* 60%) correspond to "single" Al (Fig. 1).

Changes in the source of silica did not result in a great variety of Al distribution (Fig. 2). Although the synthesis using Cab–O–Sil M5 as a silica source exhibited double the number of Al "pairs" compared to the samples synthesised using sodium silicate and TEOS, these Al "pairs" represented only 12% of all Al atoms in the zeolite and "single" aluminium atoms predominated in all samples prepared using the $Al(OH)_3$ aluminium source.

Reported results indicate that the nature and complexity of the aluminium and/or silicon source used for the synthesis of the ZSM-5 zeolite significantly affects the distribution of alumin-
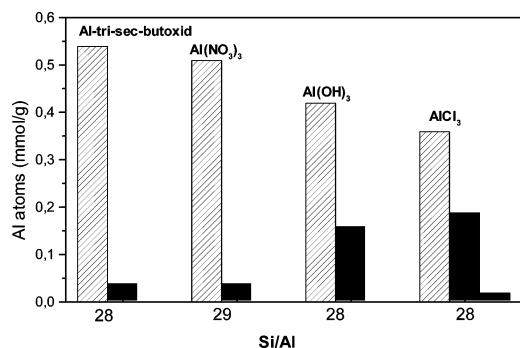

Fig. 2 Effect of the silica source on the Al distribution in ZSM-5 synthesised using $Al(NO_3)$ as the aluminium source. 'Single' Al (▨) and Al 'pairs' (■).

ium in the zeolite matrix and ZSM-5 zeolites with a well-defined distribution of aluminium atoms in a wide range of framework aluminium content can be prepared. In the case of the synthesis of ZSM-5 zeolite with tetrapropylammonium hydroxide, the nature of silica and aluminium sources and chemical reactions occurring in the synthesis gel represent parameters controlling aluminium distribution in zeolites. As significant differences in aluminium distribution were reported for commercial ZSM-5 samples[1,2] we believe that this finding can be employed with advantage for the control of aluminium distribution also in other silicon-rich zeolites. It opens the possibility for the tuning of properties of silicon-rich zeolites used as catalysts in various redox and acid reactions, and to investigate the effect of aluminium distribution on the properties and catalytic performance of these materials.

Notes and references

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Fig. 1 Effect of the aluminium source on the Al distribution in ZSM-5 synthesised using TEOS as a silica source. 'Single' Al (▨), Al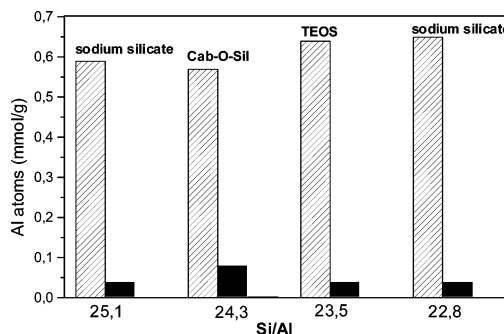 'pairs' (■) and 'close unpaired' Al (▨).