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Author(s):
Omegna, Anna

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Flexibility of the Aluminum Coordination in Alumino-Silicates. Structure of Dealuminated Zeolites and Feasibility of Realumination

Dissertation submitted to the Swiss Federal Institute of Technology (ETH) for the degree of Doctor of Technical Sciences

presented by Anna Omegna Dottore in Chimica Industriale, University of Turin, Italy

born December 16, 1972
citizen of Italy

Accepted on the recommendation of

Prof. Dr. R. Prins, Examiner
Prof. Dr. M. Hunger, Co-examiner

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Post-synthesis modifications are required to control the stability and activity of zeolite catalysts. Knowledge of the structural properties of the modified zeolites is crucial to optimize the processes leading to stable and active catalysts. The aim of this thesis is to give a comprehensive description of the modifications of the zeolite structure following post-synthesis treatments. This requires a careful characterization using a combination of techniques.

The first part of the thesis shows that, by combining $^{27}$Al (MQ) MAS NMR and Al K edge XANES spectroscopy, similarities and differences between aluminum coordinations in zeolites and amorphous silica-alumina can be revealed. Knowledge of the structure of amorphous silica-alumina is crucial for understanding the nature of the aluminum species at extralattice positions in post-synthetic zeolites. It has been shown already that the coordination of the octahedral aluminum species of protonic zeolites changes to tetrahedral upon adsorption of ammonia. This treatment is reversible, which means that the octahedral coordination is recovered when ammonia is desorbed. This led to the new concept that octahedral aluminum species exist in protonic zeolites as an inherent part of the zeolite framework. For the purpose of comparison, ammonia adsorption was carried out on amorphous silica-alumina as well as on $\gamma$-Al$_2$O$_3$ and the aluminum coordination was monitored by $^{27}$Al MAS NMR spectroscopy. The aluminum coordination in silica-alumina changed from octahedral to tetrahedral, but was unaffected in $\gamma$-Al$_2$O$_3$, indicating that the flexibility of the aluminum coordination is a general property of crystalline as well as amorphous alumino-silicates. In contrast to protonic zeolites, in which ammonia adsorption fully converts the octahedral species to tetrahedral, only a fraction of the hexacoordinated aluminum atoms in amorphous silica-alumina changes to tetrahedral, and the extent of conversion is an inverse function of the aluminum content. The effect of temperature on the aluminum coordination of silica-alumina was studied as a function of temperature by Al K edge XANES spectroscopy. This technique enables the determination of the aluminum coordination in dehydrated samples. Under moderate thermal conditions (T < 120°C), the treatment of protonic zeolites under vacuum leads to the complete conversion of the octahedral species to tetrahedral. In contrast, increasing the temperature of amorphous
silica-alumina from RT to 400°C results in a continuous conversion of the octahedral species to tetrahedral. This shows that the octahedral coordination in silica-alumina is more stable than in zeolites. This result was confirmed by $^1$H MAS NMR spectroscopy and thermogravimetric analysis. $^{27}$Al MQ MAS NMR spectroscopy revealed a difference in the quadrupolar parameters of the flexible aluminum species in protonic zeolites and silica-alumina. This can be used to distinguish flexible aluminum species in pure zeolitic and amorphous alumino-silicate frameworks. For example, the flexible aluminum coordination was studied in zeolite USY, which has a considerable portion of extraframework aluminum. Adsorption of ammonia on zeolite USY as well as thermal treatment in vacuum revealed similarities to amorphous silica-alumina as far as the behavior of the aluminum coordination is concerned. This is taken as an indication that the extraframework aluminum species in zeolite USY are associated with an amorphous silica-alumina phase.

The second part of the thesis shows that the treatment in hydrochloric acid of thermally and hydrothermally dealuminated zeolites HZSM5 does not lead to a reinsertion of aluminum into the framework, as has been reported elsewhere. Reinsertion of aluminum into the dealuminated zeolite framework is desirable in order to recover the active sites, when the goal is to produce mesoporous and highly active catalysts. After many attempts, there are still a number of unanswered questions with regard to the actual reincorporation of aluminum into the lattice. A careful investigation of the zeolites and the solution after post-synthesis must be made, in order to determine unequivocally whether reinsertion into the framework occurs. Thus, the parent HZSM5, the post-synthesis samples, as well the solutions of the acid treatment, were characterized using a combination of XRD, elemental analysis, nitrogen adsorption, FTIR, and multinuclear NMR spectroscopy. Both under thermal and hydrothermal conditions aluminum is extracted preferentially from specific crystallographic position, but the dealumination is much stronger in the presence of steam. Upon acid treatment of the thermally and hydrothermally treated HZSM5 samples, leaching of extralattice aluminum occurs as well as extraction of further structural aluminum. The reinsertion of aluminum into the lattice was not observed in any of the cases discussed here. All the treated HZSM5 zeolites, in particular the samples that were steamed and the steamed and acid-treated samples, contain large amounts of extraframework aluminum species, which constitute an amorphous silica-alumina phase generated from the reaction of aluminum and silicon in solution.
The third part of this work proposes a novel method for the realumination of a dealuminated large-pore zeolite, such as zeolite beta. If a large number of defective sites (silanol nests) form during dealumination, as is the case for zeolite beta treated with a solution of hydrochloric acid, aluminum can be reinserted at room temperature using alkoxides in an organic solvent as the aluminating agent. FTIR and $^1$H MAS NMR spectroscopy showed that Brønsted acidity was generated to an amount which was close to that in the parent material. $^{27}$Al MQ MAS NMR spectroscopy revealed that, under the reported reaction conditions, extraction as well as reinsertion of aluminum occurs preferentially at specific crystallographic positions of zeolite beta.