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Review

Coordination chemistry and reactivity of copper in zeolites

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ABSTRACT

Cu-zeolites are highly promising heterogeneous catalysts for a variety of chemical reactions. Knowledge of the location and coordination of copper in the zeolite lattice is key to fully understand its fascinating catalytic properties. Various methods exist to introduce Cu in zeolites, cation exchange being commonly used. The location of Cu in the zeolite structure has been researched for many years and an overview is presented here for the common zeolite topologies. Besides simple Cu-ion exchange, also ligated copper complexes are included in the pores and cages of zeolites. Irrespective of their introduction method, the zeolite does not merely serve as the inorganic host. As Cu interacts with the zeolite framework, while being located in a unique constraint microenvironment, a distinctly different Cu coordination chemistry often exists in the zeolites. Effects thereof on the activity of various Cu complexes are discussed in relation to oxidation chemistry and catalysis. An interesting case is the (re)activity of Cu, when exchanged in a ZSM-5 zeolite. Cu–ZSM-5 is for instance able to catalytically decompose NO_x in its elements very rapidly and, even more intriguing, recent research shows that some Cu species in Cu–ZSM-5, and by extension also in Cu–MOR, selectively oxidizes methane into methanol after activation with O_2 or N_2O. This review summarizes the latest advances and discussions on the identification of the reactive intermediates and their particular role in the reaction cycle of the methane to methanol conversion. Interestingly, recent spectroscopic and kinetic (isotopically labeled) studies on the Cu–ZSM-5 system have shed new light on the activation of small molecules on Cu-sites. The structural and mechanistic details have already been and will be very useful and instructive to understand the working fundamentals of Cu-containing biomimics and enzymes. Prof. Edward I. Solomon greatly contributed to this pioneering work.

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1. Introduction

Soon after their discovery the synthetic zeolites A, X and Y were ion-exchanged with transition metal ions (TMI) in order to modify the adsorption properties and to introduce new catalytic functionality [1–6]. A whole research area was opened with subjects such as coordination of TMI with lattice oxygen, coordination with extra-lattice ligands in confined space, immobilization of homogeneous catalysts, redox chemistry, immobilization of clusters and nanoparticles of TMI and of transition metal oxides, substitution of Al^{3+} and Si^{4+} for TMI in the zeolitic lattice and redox catalysis.

Among the TMI, copper has always been the favorite of researchers in zeolite chemistry, mainly due to its relatively simple chemistry and ease of spectroscopic detection. Copper can occur in 3 oxidation states, *viz.* II, I and 0. Copper(II) is easily detectable by relatively simple and cheap techniques such as UV–vis–NIR spectroscopy and electron paramagnetic resonance (EPR), while copper(I) has characteristic luminescence spectra.

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Quantum-chemical calculations and, especially, density functional theory (DFT) have been of key importance in the development of models of the coordination chemistry of copper in zeolites that explain the spectroscopic data.

Cu–ZSM-5 is extraordinary in that it is active in deNO_x catalysis [7–18] and in the selective hydroxylation of methane [19–21] and benzene [22–24] to methanol and phenol, respectively. Fe–ZSM-5 catalysts often closely compete for the same reactions [25,26]. Cu–ZSM-5 and Fe–ZSM-5 differ in catalyst activation and in reaction temperature. Both catalysts are activated by heating at high temperatures in inert atmosphere. For Fe–ZSM-5 this treatment is followed by activation in N_2O, while for Cu–ZSM-5 activation in O_2 and N_2O is possible. The selective oxidation of methane typically occurs at room temperature with Fe–ZSM-5 and in the range of 373–473 K for Cu–ZSM-5. Soluble methane mono-oxygenase (sMMO) with Fe in its active core and particulate methane mono-oxygenase (pMMO) with Cu in its active core are the enzymatic counterparts of Cu– and Fe–ZSM-5 [20,26,27]. Recently Hammond et al. reported on a bimetallic zeolite, *viz.* Fe–Cu–ZSM-5, that is active for the selective oxidation of methane to methanol with aqueous hydrogen peroxide. The addition of Cu to an Fe–ZSM-5 catalyst increased the methanol selectivity due to a synergetic effect between copper and iron, whereby copper merely overcomes the formation of hydroxyl radicals and the methanol over-oxidation coupled thereto [28].

In this review we mainly concentrate on the coordination chemistry of copper in zeolites with the following subjects: ion exchange, coordination to lattice oxygen, coordination of extra-framework ligands, deNO_x catalysis and the selective oxidation of methane into methanol. Many reviews have been published over the years and our own reviews are referenced for the interested readers that want more detailed information [29–32].

2. Ion exchange and coordination to lattice oxygen

The classical method of preparation of a Cu-zeolite is ion exchange of $[Cu(H_2O)_6]^{2+}$ from aqueous solution into the pore system of zeolites. The pH in the pores must be below the pH of precipitation of Cu^{2+} in aqueous solution, which is 6 at $[Cu^{2+}] = 0.01$ M [33]. As the pH in the pores is unknown, it is recommendable to keep the pH of the exchange solution below 6. As a consequence, exchange of a few protons accompanies Cu^{2+} exchange, giving rise to acidic bridging hydroxyl groups. If the pH in the pores is too high, Cu^{2+} precipitates in the pores and over-exchanged zeolites are obtained. These zeolites contain more Cu^{2+} than needed for neutralization of the cation exchange capacity (CEC) or the Cu/Al ratio exceeds 0.5 [34].

Solid state ion exchange consists of the heating of a mixture of a zeolite and a predetermined amount of a cupric or cuprous ion salt. The following reactions occur:

$$CuX_2 + Na_2\text{-}Z \rightarrow Cu\text{-}Z + 2NaX \quad (1)$$

$$CuX_2 + H_2\text{-}Z \rightarrow Cu\text{-}Z + 2HX \quad (2)$$

Z represents a zeolite and X a monovalent anion. Similar reactions can be written for Cu(I) exchange. The formed salt NaX is either removed with the gas flow during the solid state exchange or it must be removed after exchange by washing. In the first case the boiling point of the salt is below the exchange temperature. HX is an acid. It is desorbed in the gas phase at high temperatures during the ion exchange. It may attack the lattice, leading to local zeolite lattice destruction, especially if water is desorbed simultaneously.

The obtained Cu-exchanged zeolites are calcined to remove physisorbed water and water in the first coordination sphere. Cu^{2+} coordinates now with the lattice oxygen atoms in the zeolite channels and cages. The siting has been studied with X-ray diffraction

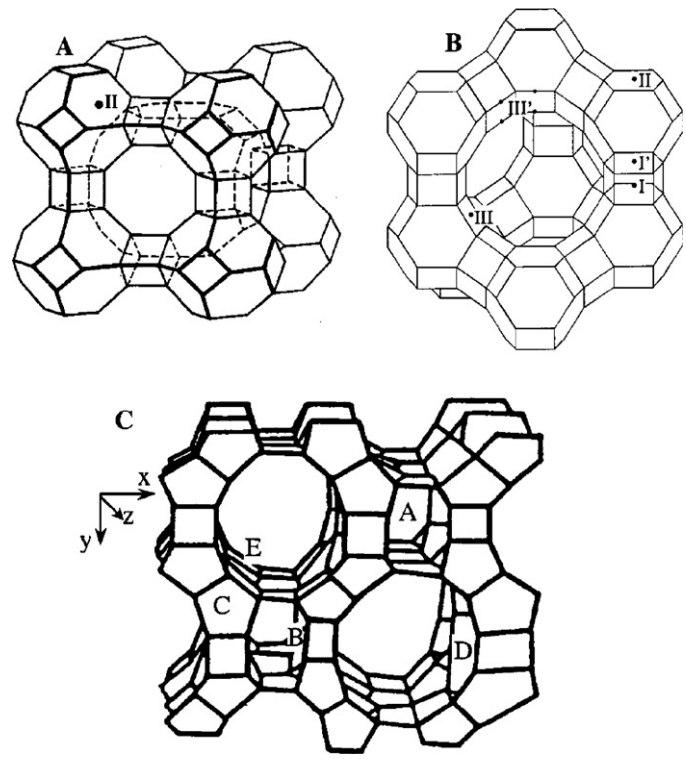

Fig. 1. Schematic framework structure of zeolite A, ZK4 (A), zeolite X, Y (B) and mordenite (C); only the T atoms are shown on the vertices of the structure, the oxygen atoms are arranged in between; the location of the exchangeable cation sites is also indicated; the contours of the supercage in zeolite A are shown by dashed lines [36].

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(XRD) and the sites and their occupancy have been tabulated by Mortier [35]. The sites are indicated in Fig. 1 for various zeolites such as A, X, Y and mordenite. These data show that the sites are well established crystallographically for the low silica zeolites, much less so for high silica zeolites such as the mordenite and ZSM-5.

In dehydrated zeolites the six-ring of oxygen atoms or six-membered ring (6MR) is the most favorable coordination environment of Cu^{2+}, coordinating with 3 oxygen atoms of the 6MR. The point group of this $[CuO_3]$ unit is D_{3h}, if Cu^{2+} resides in the plane of the 3 oxygen atoms, and C_{3v} if Cu^{2+} is located slightly above the plane of the 3 oxygen atoms. This coordination environment has been probed by UV–vis–NIR spectroscopy and EPR. The UV–vis–NIR spectra reveal weak d–d transitions in the region 9000–15,000 cm^{-1} and an intense, broad, unresolved charge transfer (CT) band in the 40,000–45,000 cm^{-1} region. For low silica zeolites such as zeolites A, X, Y and chabazite, 3 d–d transitions are distinguished with maxima around 10,500–11,000 cm^{-1}, around 12,500 cm^{-1} and 14,500 cm^{-1}, the first one being the most intense signal. For high silica zeolites such as mordenite and ZSM-5 the d–d band maximum is around 13,600 cm^{-1} and the different d–d components are only partially resolved [37–40]. For all the zeolites, except zeolite A, two axially symmetric EPR signals of Cu^{2+} are clearly resolved. The EPR parameters are summarized in Table 1. The hyperfine signals are clearly resolved in the parallel region, but only partially resolved in the perpendicular region.

The two characteristic $g_{||}$ parameters for the low silica zeolites are $g_{||} = 2.36$–2.40 and $g_{||} = 2.32$–2.35. The siting has been done with O_2 line broadening experiments. The signals that disappear in the presence of O_2 are due to copper in sites that are accessible to O_2. These are the 6MR's in the supercages of zeolites A, X and Y and in the cages of erionite, chabazite and zeolites T and L. They are the sites II in Fig. 1, and they are accessible *via* windows consisting

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