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Mendeleev Commun., 2016, **26**, 254–255

Mendeleev Communications

Water as a key factor providing an easy migration/redistribution of Cu^{2+} species in CuO/HZSM-5

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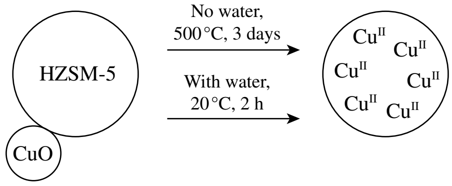
DOI: 10.1016/j.mencom.2016.05.011

The presence of liquid water or even water vapor facilitates drastically the migration/redistribution of Cu^{2+} ions in the low-loaded hybrid system CuO/HZSM-5.



The Cu-HZSM-5 system representing a specific type of hybrid materials[1] is widely investigated for many years due to its unique ability to catalyze NO decomposition, selective catalytic reduction of NO_x, and total alkane oxidation.[2–4] Characterization of Cu-HZSM-5 by physical methods often yields contradictory data on changes in the coordinative and valence states of copper in the Cu-ZSM-5 treated under different conditions.[5–7] The mechanism of Cu-HZSM-5 deactivation upon high-temperature treatment of the catalysts is also not fully understood.[8,9] Results obtained by different researchers contain a lot of both similarities and discrepancies in properties of the Cu-HZSM-5 depending on the preparation/treatment methods mainly. Little attention was paid earlier to the specific role of water always being present in the system.[10] Thus, a question arises: is not it the water playing an important role in the redistribution of cupric species in the zeolitic channels? If water can provide an easy migration of hydrated species at low temperatures, as distinct from 'naked' Cu^{2+} ions in dry high-temperature samples, such a water-assisted redistribution can explain a major part of discrepancy in the data.

Peculiarities of introduction of Cu^{II} ions in cationic positions of HZSM-5 and properties of these ions were studied in detail previously[11,12] and the method for the quantitative determination of isolated ions in Cu-HZSM-5 by ESR was proposed.[13,14] It was demonstrated that, in the cation-deficient low-loaded sample, 0.5% Cu/HZSM-5, all Cu^{2+} ions remained well isolated and contributed to the ESR signal.[14] Thus, ESR spectroscopy is a sensitive and informative method for study of just such diluted system.

The aim of this work was to monitor, by ESR, peculiarities of stabilization and redistribution of isolated cupric ions in HZSM-5 as a function of the treatment of the hybrid system 0.5% CuO/HZSM-5 in the presence of a controlled amount of water.

Calcined powder of CuO and air-dried powder of precipitated copper hydroxide were placed in ESR ampoules and the spectra of these compounds were measured at –196 °C.[†] A trace ESR signal can be hardly discerned only, and no other lines are present in the spectra. This is an important point in ESR monitoring of further transformations of the hybrid CuO/HZSM-5 system. So, the number of isolated cupric ions or weak irregular associates is negligible in both compounds, and all the Cu^{2+} ions in starting CuO and $Cu_2(OH)_2NO_3\cdot 1.4\,H_2O$ are aggregated into three-dimensional crystals demonstrating a strong magnetic interaction between paramagnetic Cu^{II} ions. These data agree well with XRD results confirming a good cristallinity of starting compounds mixed with zeolite.

Copper nitrate $Cu(NO_3)_2\cdot 3H_2O$ of chemically pure grade was used for ion exchange with zeolite and preparation of copper oxide and hydroxide samples. Copper oxide was prepared by calcination of nitrate at 500 °C for 4 h in an airflow. Black powder prepared demonstrated good XRD crystallinity.

A fresh precipitate of $Cu_2(OH)_2NO_3$ was prepared by addition of an NH_4OH solution (Fisher Scientific) to the solution of copper nitrate until neutral pH. The blue precipitate was filtered and washed with distilled water and then dried on air at 20 °C for 2 h. X-ray pattern of the precipitate demonstrated that copper hydroxide nitrate with orthorhombic structure and good crystallinity was obtained. The total water loss (35.2 wt% up to 500 °C) during DTA analysis of the air-dried powder showed that the sample can be described by the formula $[Cu_2(OH)_2NO_3\cdot 1.4\,H_2O]$.

Hybrid samples. The weighed amounts of HZSM-5 and air-dry CuO or $[Cu_2(OH)_2NO_3\cdot 1.4\,H_2O]$ powder were mixed/ground in a mortar, by a pestle, for 10 min. The powders obtained were pressed into pellets, crushed, and the fraction 0.5–1 mm was prepared for further investigations. The amount of copper in the zeolite (0.5 wt% Cu) was chosen to deal with cation-deficient samples. For the zeolite used, the atomic ratio Cu/Al comes to ~0.123, *i.e.*, is far below the stoichiometry. Prepared earlier by incipient wetness impregnation sample 0.5% Cu-HZSM-5 pre-calcined at 520 °C was used for comparison.

ESR measurements. Samples were placed in quartz ESR ampoules and treated in two modes: (1) repeated calcination in air at 500 °C → evacuation at 20 °C → ESR measurement at 20 or –196 °C; (2) impregnation with distilled water at 20 °C → repeated ESR measurements at –196 °C.

The Cu^{2+} ESR spectra were taken in the X-band ($\lambda \cong 3.2$ cm) at 20 and –196 °C on a spectrometer equipped with a 4104OR cavity and a co-axial quartz Dewar. The ESR signals were recorded in the lack of saturation at the modulation amplitude 4.0 G in a field range of 2000–4000 G. Concentration of isolated copper(II) ions was evaluated by double-integration of the asymmetric well-resolved ESR signal with $A_{\|} = 132$ G, $g_{\|} = 2.38$, and $g_{\perp} = 2.08$, being typical of Cu^{2+} species in near-octahedral coordination. For better accuracy of the ESR quantitation of Cu^{2+}, the standard (sealed ampoule with copper nitrate solution in ethanol) was used as a reference.

[†] *HZSM-5.* The H-form of ZSM-5 (Si/Al = 25; crystallinity of >90%; PQ Corporation) was pre-calcined in an airflow at 520 °C.

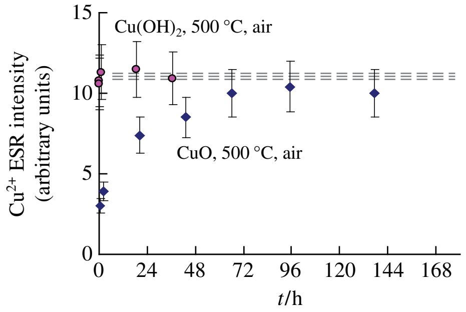


Figure 1 Dynamics of appearance of ESR-observable isolated Cu^{2+} cations upon calcination of mechanical mixtures of CuO/HZSM-5 and [$Cu_2(OH)_2NO_3 \cdot 1.4H_2O$]/HZSM-5 at 500 °C.

Starting mixture of black CuO and white HZSM-5 has a gray color and shows a trace ESR signal from isolated Cu^{2+} ions. Calcination of the sample at 500 °C leads to a gradual increase in the concentration of isolated ESR-visible Cu^{2+} ions reaching the limit in about three days (Figure 1). At the same time, the color of the sample becomes white with a slight blue tone. The maximal ESR intensity reached coincides with the one measured for the reference sample 0.5% Cu-HZSM-5 prepared by impregnation/calcination and containing only ESR-visible isolated copper cations. Thus, complete 'dry dissolution' of CuO in HZSM-5 demands three days at 500 °C. From chemical point of view, the process looks as dissolution of copper oxide by strong acid (Brønsted zeolitic sites of HZSM-5). Therefore, the reaction $CuO + 2H^+ \rightarrow Cu^{2+} + H_2O$ provides a driving force of the process in any case. However, under dry conditions, this solid-state reaction is strongly hindered and ion migration process is very slow.

The use of the copper hydroxide powder instead of CuO changes the situation drastically. Mechanical grounding of HZSM-5 with air-dry Cu hydroxide powder at room temperature for 10 min results in appearance of measurable ESR signal typical of isolated copper(II) ions. Heating of the sample in closed ampoule at 100 °C for a few minutes causes a noticeable increase in the signal intensity. Subsequent calcination at 500 °C for 1–2 min leads to formation of strong ESR spectrum from isolated Cu^{2+} ions with integral intensity corresponding to 100% of copper added to zeolite (Figure 1).

Impregnation of the mechanical mixture CuO/HZSM-5 with distilled water at 20 °C is accompanied by fast rise of concentration of ESR-visible isolated cupric ions (Figure 2) and color change from dark gray to light blue. Therefore, in the presence of liquid water dissipation of CuO particles into the HZSM-5 matrix lasts only 1–3 h at room temperature (see Figure 2).

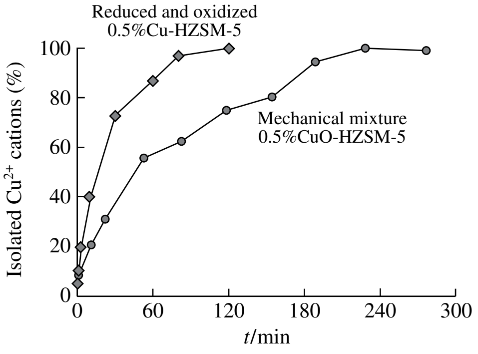


Figure 2 Kinetics of appearance of ESR-observable isolated Cu^{2+} cations after impregnation of samples with distilled water at room temperature.

One more experiment, with a redox cycle of 0.5% Cu-HZSM-5 treatment, was repeated with water assistance at the step of reoxidation. Reduction of preoxidized sample by H_2 (300 °C, 2 h) resulted in complete disappearance of Cu^{2+} ESR signal due to quantitative metal reduction and formation of Cu^0 microcrystals (~15 nm according to XRD data) on the outer zeolitic surface. Second step of oxidation of the sample by dry air at 300 °C provides transformation of metallic particles into particles of CuO but without appearance of isolated Cu^{2+} ions. However, the subsequent impregnation of the sample at 20 °C with distilled water provokes fast transformation of all the copper into isolated ESR-visible Cu^{2+} species (see Figure 2). The same complete dissipation of CuO to isolated Cu^{2+} ions under dry conditions demands ~24 h of calcination at 500 °C. Therefore, distribution of components in CuO/HZSM-5 hybrid system seems to become very flexible in the presence of such strong ligand as water. Not only a liquid water but also even water vapor facilitates drastically migration of cupric species to strong acidic sites inside zeolitic channels.

Water provides a surprisingly easy migration of hydrated cupric species in HZSM-5 channels at low temperatures, which can explain a major part of discrepancy in the data being received for the Cu-HZSM-5 system.

This study was supported by the Russian Science Foundation (grant no. 14-50-00126).

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Received: 21st August 2015; Com. 15/4713