Solid-State Ion-Exchange of Copper into Zeolites Facilitated by Ammonia at Low Temperatures

Soran Shwan1, Magnus Skoglundh1, Lars F. Lundegaard2, Ramchandra R. Tiruvalam1, Ton V. W. Janssens1 and Anna Carlsson1 and Peter N. R. Vennestrøm1,2

1 Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden, 2Research & Development Division, Haldor Topsoe A/S, Nymøllevej 55, DK-2800 Kongens Lyngby, Denmark.

Introduction

Copper-exchanged zeolites offer promising perspectives to many technological applications. An example is the selective partial oxidation of methane to methanol over e.g. Cu-MFI or Cu-FER [1,2]. The catalytically active sites have been identified as copper dimers ([Cu2O]3+ and are typically obtained in “over-exchanged” zeolites where Cu/Al ratios > 0.5. Another and already implemented use of Cu-exchanged zeolites is for the reduction of nitrogen oxides in the exhaust from diesel fuelled vehicles through selective catalytic reduction using ammonia as a reducing agent (NH3-SCR): 4NH3 + 4 NO + O2 → 2 N2 + 6 H2O [3].

By changing the gas atmosphere, the SSIE process can occur at lower temperatures. Previous results have shown that heating a mixture of CuO and an MFI zeolite in an atmosphere of NO, NH3, O2, H2O, and N2 at 550 °C results in levels of exchanged Cu similar to those obtained by aqueous ion-exchange [4]. We show here that SSIE of Cu already occurs at 250 °C, by heating dry mixtures of copper oxides and zeolites in the presence of NH3 and optionally NO. The Cu migration into the zeolites is confirmed by scanning transmission electron microscopy (STEM) imaging and in situ X-ray diffraction (XRD) shows the migration of Cu to the formation of a CuO oxide phase.

Materials and Methods

Powder mixtures of copper oxides (CuO or Cu2O) and zeolites (CHA, MFI and BEA) were treated in various combinations of NO, NH3, O2, H2O and N2. The efficiency of the SSIE was followed measurement of the NO conversion in the NH3-SCR reaction, which is possible since SSIE of Cu in zeolites result in active SCR catalysts. Furthermore, STEM imaging was used to confirm the Cu migration and in situ XRD was used to identify the Cu phases present during the SSIE process.

Results and Discussion

It is found that NH3 is the critical gas-phase component that allows for low-temperature SSIE in dry mixtures of Cu oxides in zeolites. When CuO is used, NO enhances the SSIE process. The catalytic activity of materials obtained by (NH3+NO)-SSIE with CuO after 5 h is comparable to those prepared with aqueous ion exchange. In situ XRD reveals that the SSIE process is related to the formation of Cu2O and that addition of NO to the NH3 atmosphere enhances the formation of Cu2O. However, some CuO can be formed as well, which impedes further exchanges by SSIE (Figure 1). When CuO is used in the mixture, NO is not required and reduction to Cu2 is avoided. The SSIE can then continue and leads to materials with a higher degree of copper exchange. This can be seen by the change in zeolite lattice parameters (Figure 1), and by an even further increase in catalytic activity.

The ability to form [Cu3(NH3)4]2+ complexes is proposed to be the reason for the possibility of low-temperature migration of Cu into the zeolite exchange positions. As the migrating species is in the Cu2 state, this procedure allows, in principle, for simple preparation of materials with Cu/Al ratios up to 1.0.

Figure 1. Quantitative Rietveld analysis during SSIE of various copper phases into an MFI zeolite in an atmosphere of NO+NH3 or NH3 only. Left: Phase fractions of zeolite and Cu2O. Right: Evolution of zeolite lattice parameters during the treatments.

Significance

Solid-state ion-exchange from copper oxides into zeolites is shown to be possible at unprecedented low temperatures (< 250 °C) when facilitated by ammonia. The mobility of Cu at low temperatures is proposed to be related to the formation of [Cu3(NH3)4]2+ complexes that allow for simple preparation of over-exchanged zeolites with Cu/Al ratios > 0.5.

References