



	Experiment title: Interaction of ionic liquids with immobilized metal nanoparticles and organometallic complexes	Experiment number: CH-2691
Beamline: BM26A	Date of experiment: from: 3.10.2008 to: 8.10.2008	Date of report: 26.02.2009
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Report:

Introduction

Ionic liquids are a class of novel solvents with extremely high polarity [i]. Immobilization of organometallic complexes and metal nanoparticles in thin films of supported ionic liquid has been suggested as a novel concept to combine the high selectivity of homogeneous catalysts with the easy separation of a heterogeneous system [ii]. By using this concept complex catalysts can be assembled from well-characterized and well-defined building blocks. Supported ionic liquids are an ideal medium for reactions with strong interactions of reactants and products. The use of ionic liquids also prevents oxidation of supported metal particles, mediates interactions with reactants and products and also allows tuning the solubility of reactants.

The question arises, however, to what extent the highly polar ionic liquid influences the structure and properties of the metal organic complex and how the ionic liquid is influenced by the presence of metal nanoparticles. In order to understand these effects and their influence on the activity and selectivity of the catalysts, it is essential to study the nature of the interaction between the active component and the ionic liquid.

Experimental

As support material different aluminum-oxides, differing in pore-volume and specific surface area were used. The alumina was dried at 200 °C for two hours before use. Catalysts with immobilized metal clusters (5 wt% metal) were prepared by incipient wetness impregnation. Copper(II) nitrate trihydrate was dissolved in the appropriate amount of bi-distilled water; the solution was trickled onto the support and stirred until the water was completely absorbed. The water was removed by freeze drying. The precursors were calcined at 300 °C for three hours and at 450 °C for four hours in synthetic air.

For preparing the supported ionic liquid catalysts Cu/Al₂O₃ was added to a solution of BDiMIm (1-butyl-2,3-dimethyl-imidazolium trifluoromethane sulphonate) dissolved in methanol. The suspension was stirred at

room temperature for 10 min and the volatile components were slowly removed by freeze drying to give a free flowing black powder (Cu/BDiMIm/Al₂O₃).

XAFS experiments were performed at beamline BM26A. The catalysts were pressed into self supporting wafers (ca. 100 mg) and placed into an *in-situ* XAS cell that can be cooled to liquid nitrogen temperature using a recycle dewar and heated to 400 °C using a sealed heating wire. The X-ray absorption spectra were collected at the Cu K edge (8979 eV) in a helium flow at liquid N₂ temperature. The EXAFS data was analyzed using the *Viper* software.ⁱⁱⁱ For EXAFS analysis, the scattering contributions of the background were removed from the X-ray absorption by a third-order polynomial function. The oscillations were weighted with k^2 and Fourier-transformed within the limit $k = 3.5\text{--}13 \text{ \AA}^{-1}$. The local environment of the Cu atoms was determined from the EXAFS using the phase-shift and amplitude function for Cu–Cu and Cu–O calculated assuming multiple scattering processes (FEFF version 8.40).^{iv,v} The XANES data were collected in a helium flow at room temperature or during activation in hydrogen and analyzed using the *XANES dactyloscope* software.^{vi} All recorded XANES spectra were normalized to unity.

Results

The uncoated catalysts (see Tab.1) were activated *in-situ* at 250 °C for 30 minutes. During cool down the cell was flushed with helium. Afterwards XANES (Fig. 1, at room temperature) and EXAFS (at LNT) were recorded. The analysis of the XANES data showed that the copper particles on the supports with a surface area smaller than 100 m²/g were in oxidation state zero (pre-edge feature at 8980 eV and local maximum at 9025 eV).

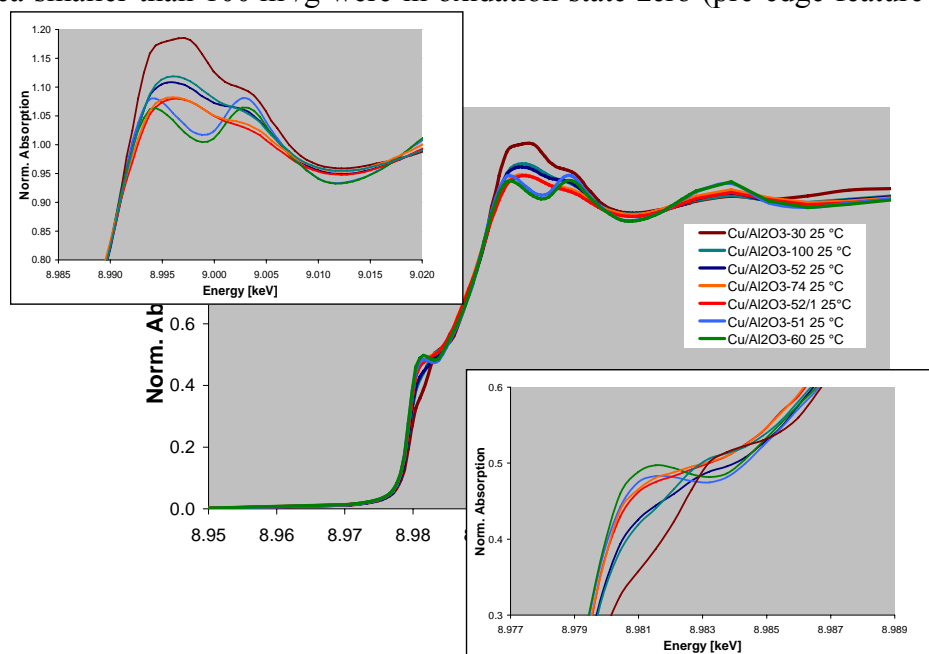


Figure 1: XANES of different uncoated copper catalysts

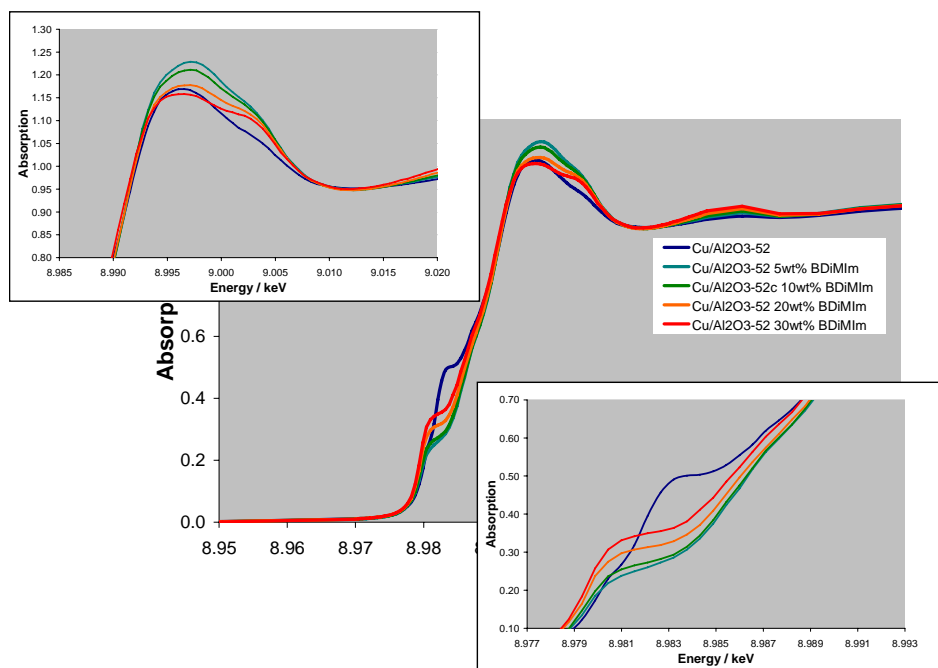
neighboring atoms, the dispersion and the particle size based on cuboctahedral particles are listed in Tab. 1.

Tab 1: Results of EXAFS analysis (particle size calculation based on cuboctahedral particles with 147 atoms)

Catalyst	Surface area [m ² /g]	Cu-O R[Å] (CN)	Cu-Cu 1. Shell R[Å] (CN)	Dispersion	Cu particle size [nm]
Cu/Al ₂ O ₃ -60	54	---	2.54 (9.2)	0.59	2.1
Cu/Al ₂ O ₃ -51	99	---	2.55 (8.8)	0.63	2.0
Cu/Al ₂ O ₃ -52/1	149	1.84 (0.4)	2.53 (6.9)	0.82	1.2
Cu/Al ₂ O ₃ -74	151	1.84 (0.4)	2.53 (6.9)	0.82	1.2
Cu/Al ₂ O ₃ -52	214	1.86 (0.6)	2.53 (6.1)	0.87	1.0
Cu/Al ₂ O ₃ -100	257	1.87 (0.7)	2.52 (7.0)	0.81	1.3
Cu/Al ₂ O ₃ -30	360	1.92 (2.2)	2.53 (4.6)	0.93	0.9

Activity tests performed in the low temperature water gas shift reaction, showed highest conversions of CO

for catalysts with 0.4 neighboring oxygen atoms, i.e. a degree of reduction (relative to the Cu(0) and the Cu(I) reference foil) of ca. 75 %. The dependency of the activity on the dispersion and the degree of reduction shows that a balanced amount of Cu(I)O must be present to stabilize highly dispersed Cu(0) particles. With increasing amount of Cu(I) the obtained particle size is very small, but the active centers are blocked by copper oxide. A higher degree of reductions leads to bigger particles and thus a lower dispersion.



Furthermore the influence of ionic liquid on the reduction temperature was explored. Fig. 2 shows the XANES of catalysts coated with 0 to 30 wt.% ionic liquid. The spectra were recorded at 210 °C under a hydrogen flow. A higher amount of ionic liquid leads to a higher degree of reduction, which can be attributed to the fact that the water produced during the reduction process is absorbed by the ionic liquid and thus increasing the speed of the reduction.

Fig 2: XANES of catalysts coated with 0 to 30wt.% BDiMIm

Conclusions

Copper catalysts for the low temperature water gas shift reaction were examined by EXAFS and XANES to investigate the influence of the support material as well as the influence of a coating with ionic liquid on the reduction properties. The results indicate that catalysts with a balanced amount of Cu(I)O, needed to stabilize highly dispersed Cu(0) particles, show highest activities in the catalytic tests. A coating with ionic liquid leads to a lower reduction temperature due to the absorbance of water into the ionic liquid film.

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