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## ***In situ* XAS study of supported CuNi-catalyst for CO hydrogenation**

Gian Luca Chiarello<sup>1</sup>, Qiongxiao Wu<sup>2</sup>, Jakob M. Christensen<sup>2</sup>, Burcin Temel<sup>3</sup>, Alexey Boubnov<sup>1</sup>, Matthias Bauer<sup>1</sup>, Anker D. Jensen<sup>2</sup> and Jan-Dierk Grunwaldt<sup>1\*</sup>

<sup>1</sup>*Institute of Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Engesserstr. 20, 76131 Karlsruhe (Germany)*

<sup>2</sup>*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads, Building 229, 2800 Kgs. Lyngby (Denmark)*

<sup>3</sup>*Haldor Topsøe A/S, Nymoellevej 55, 2800 Kgs. Lyngby (Denmark)*

\*E-mail address: grunwaldt@kit.edu

### ***Introduction***

The synthesis of higher alcohols (C<sub>2+</sub> alcohols) from synthesis gas has received a renewed attention in the last years for its application in the field of biofuel and bioadditive production [1-2]. Indeed, synthesis gas can be successfully produced by gasification of biomass waste. Among other transition metals, Ni/Cu based catalysts are promising candidates for the title reaction. This work provides a comparison of catalytic activity results and *in-situ* X-ray absorption spectroscopic (XAS) investigations of CuNi/Al<sub>2</sub>O<sub>3</sub> and CuNi/CNTs (Carbon Nanotubes) to elucidate: *i*) the Cu/Ni structure after reduction and *ii*) the effect of the support.

### ***Experimental***

10wt%Cu/10wt%Ni deposited on CNTs (Sigma-Aldrich) or Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by impregnation of Cu and Ni nitrates, followed by overnight drying at 120°C and annealing in air or N<sub>2</sub> (CNTs based cats.) at 400°C for 4 h. The so obtained catalysts have been characterized by BET, HRTEM, *in-situ* XRD, QMS-TPR and *in-situ* XAS at the Ni K- and Cu K-edges both during reduction and exposure in syngas. The XAS experiments were performed with a recently installed *in-situ* setup at the synchrotron of Karlsruhe ANKA-XAS beamline [3]. Catalytic tests were performed in a fixed-bed continuous-flow reactor [2]. Prior to the reaction, the catalysts were pre-reduced under flowing 10% H<sub>2</sub>/N<sub>2</sub> mixture for 12 h at 300 °C. Typical operating conditions are: P = 60-100 bar; T = 250-325 °C; GHSV = 2000 h<sup>-1</sup>; Feed: H<sub>2</sub>/CO=1 (v/v).

### ***Results/Discussion***

The two samples display different QMS-TPR profiles: a single-broad peak centred at 200 °C for the CNT supported catalyst (Fig.1) and a doubled peak at 212 and 230°C for the Al<sub>2</sub>O<sub>3</sub> supported sample. *In-situ* XANES (Fig.1) show that both Ni and Cu start to reduce almost simultaneously at ca.180 °C on the former catalyst, whereas Ni on Al<sub>2</sub>O<sub>3</sub> starts to reduce at

higher T than Cu. However, on both samples Cu rapidly fully reduces, whereas Ni displays a slower reduction profiles along T and at 300°C a significant fraction of Ni still retains the oxidised state. These results suggest that Ni is present in different forms *i.e.* partially alloyed with Cu, which reduces at lower T, together with NiO and very likely NiAl<sub>2</sub>O<sub>4</sub> in the case of the alumina supported sample [4], which are reduced at higher temperature. *In-situ* EXAFS spectra recorded under flowing syngas at 300°C revealed no changes in the copper particles but some variation in the structure of nickel.

Figure 1. *in-situ* XANES spectra at the Cu K-edge during reduction up to 300 °C (left panel) and fraction of oxidised Cu and Ni obtained by linear combination of the *in-situ* XANES spectra together with QMS-TPR profile (right panel) over the CuNi/CNTs sample.

Table 1 shows that Cu-Ni catalysts supported on Al<sub>2</sub>O<sub>3</sub> and CNTs exhibited different catalytic behaviors for CO hydrogenation [5]. The CNTs supported catalyst showed higher activity than the Al<sub>2</sub>O<sub>3</sub> supported one. These results are interpreted on the basis of Lewis acidic sites of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and strong interaction between Ni and Al<sub>2</sub>O<sub>3</sub> which hinders the formation of the active Cu/Ni alloy. The current work is focused on changing the catalytic selectivity towards higher alcohols by modifying the basicity of the catalysts with alkali and other promoters.

Table 1. Catalytic results of CuNi-based catalysts in CO hydrogenation at 300°C and 100 bar

Catalyst	CO conv. / mol%	Carbon based selectivity / mol%			
		Alcohols	Oxygenates	Hydrocarbons	CO <sub>2</sub>
CuNi/Al <sub>2</sub> O <sub>3</sub>	27.9	4.4	34.4	12.7	48.5
CuNi/CNTs	37.6	77.6	3.4	6.7	12.3

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