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1. Introduction

Cu–Ni alloys are widely used as catalysts in, for example, steam reforming,^{1–6} dimethyl carbonate synthesis,^{7–9} hydrodeoxygenation,^{10–12} water gas shift,^{13–17} CO₂ hydrogenation,^{18,19} and CO hydrogenation.^{20–23} The chemical and physical properties of Cu–Ni alloys as well as the catalytic properties of the alloys have been described extensively in the literature. However, the structure of supported Cu–Ni catalysts is still unclear. With respect to bulk Cu–Ni alloy formation, the phase diagram of the binary Cu–Ni system shows phase segregation for a broad range of mixing ratios at room temperature^{24,25} and formation of a solid solution only above a certain critical temperature, typically found in the 200–300 °C range depending on the alloy composition.^{24–27} Regarding the supported Cu–Ni system,

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Silica supported Cu-Ni (20 wt% Cu + Ni on silica, molar ratio of Cu/Ni = 2) alloys are prepared *via* impregnation, coprecipitation, and deposition-coprecipitation methods. The approach to co-precipitate the SiO₂ from Na₂SiO₃ together with metal precursors is found to be an efficient way to prepare high surface area silica supported catalysts (BET surface area up to 322 m² g⁻¹, and metal area calculated from X-ray diffraction particle size up to 29 m² g⁻¹). The formation of bimetallic Cu-Ni alloy nanoparticles has been studied during reduction using *in situ* X-ray diffraction. Compared to impregnation, the coprecipitation and deposition-coprecipitation methods are more efficient for preparation of small and homogeneous Cu-Ni alloy nanoparticles. In order to examine the stability of Cu-Ni alloys in high pressure synthesis gas conversion, they have been tested for high pressure CO hydrogenation (50 bar CO and 50 bar H₂). These alloy catalysts are highly selective (more than 99 mol%) and active for methanol synthesis; however, loss of Ni caused by nickel carbonyl formation is found to be a serious issue. The Ni carbonyl formation should be considered, if Ni-containing catalysts (even in alloyed form) are used under conditions with high partial pressure of CO.

it was found that homogeneous alloys only formed when the Cu-Ni alloys were rich in Ni.13,28 Similarly, on the basis of in situ X-ray diffraction (XRD) analysis, we recently found that silica supported Cu-Ni alloys prepared via impregnation formed a homogeneous solid solution of Cu and Ni at high nickel concentrations.²⁹ At lower nickel content, there is a segregation into metallic Cu and Cu-Ni alloy.²⁹ In that case, the particle size was found to decrease significantly with increasing Ni content, and the phase segregation seen for Cu-rich compositions might be partly caused by the larger metal particle size in the Cu-rich range. The particle size has in some cases been found to be an important parameter for alloy formation.²⁹⁻³¹ For example, bimetallic, bulk Cu-Ag shows phase segregation for a broad composition range, but when the clusters are smaller than a critical size (ca. 1 nm), there is no phase segregation at all.³⁰ It has been reported that preparation of metal particles from nitrate precursors via impregnation generally leads to significantly larger metal particles than preparation by, for example, co-precipitation.³²⁻³⁵ Cu-based catalysts are often prepared by a co-precipitation approach since high metal loadings can be achieved in combination with high metal dispersion (small particles) and improved stability.³⁶⁻³⁸ In this work, we have investigated the effect of preparation methods on Cu-rich, Cu-Ni (Cu/Ni = 2/1, molar ratio) alloy formation on a silica support. We have prepared



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Influence of preparation method on supported Cu–Ni alloys and their catalytic properties in high pressure CO hydrogenation

silica supported Cu–Ni catalysts *via* three different preparation methods: incipient wetness impregnation, coprecipitation and deposition–coprecipitation. The aim was to evaluate if precipitation methods would be able to yield homogeneous alloys also in the Cu-rich composition range, where this is difficult to achieve using impregnation methods. If this can be achieved, it could potentially be of importance in many of the applications of Cu–Ni catalysts. Different characterization techniques such as *in situ* XRD, BET surface area measurements, thermogravimetric analysis (TGA) and transmission electron microscopy (TEM) have been used to evaluate the structure of the supported Cu–Ni systems.

Furthermore, Cu-Ni alloys have, as touched upon above, attracted attention as catalysts for CO hydrogenation. Cu-Ni catalysts have been reported to hydrogenate CO to different products such as higher alcohols,^{39,40} hydrocarbons,²¹ and methanol.^{23,41-44} It is known that metallic Ni in the presence of CO could form the volatile carbonyl Ni(CO)₄, which could cause Ni particle sintering and loss of Ni under certain conditions.⁴⁵⁻⁴⁷ However, the influence of Ni carbonyl formation has not been studied in our own previous work on this system⁴³ or in the general literature^{20-23,44} on high pressure CO hydrogenation over Cu-Ni catalysts. It remains unknown whether Ni in the Cu-Ni alloys can be removed with the effluent syngas stream. It would thus be important to determine if there is any Ni loss due to carbonyl formation. In order to examine the stability of Cu-Ni, we have tested the Cu-Ni catalysts in high pressure CO hydrogenation, and subsequently analyzed the composition of both fresh and spent catalysts by elemental analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES).

2. Experimental section

2.1 Preparation of Cu-Ni precursor materials

Silica supported Cu–Ni catalyst precursors (20 wt% Cu + Ni, Cu/Ni = 2 molar ratio) were prepared by incipient wetness impregnation, coprecipitation, and deposition–coprecipitation. The specific preparation procedures are described below.

Incipient wetness impregnation. An aqueous solution was prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich) in demineralized water. Silica particles (600–1400 µm, with a BET surface area of 207 m² g⁻¹, supplied by Saint-Gobain Norpro) were impregnated with an amount of the aqueous solution corresponding to the pore volume of the support (1.2 ml g⁻¹ for SiO₂). After 1 h aging at room temperature, the catalyst precursors were dried at 110 °C in air overnight. This sample was denoted as Cu–Ni/SiO₂–IWI.

Coprecipitation. An aqueous solution of mixed metal nitrates $[(Cu(NO_3)_2 \cdot 3H_2O (0.0690 \text{ M}) \text{ and } Ni(NO_3)_2 \cdot 6H_2O (0.0345 \text{ M}), 250 \text{ m}]]$ with 25 ml of 37 wt% HNO₃ was coprecipitated using a solution of Na₂Si₂O₃ (Sigma-Aldrich, 500 ml, 0.213 M) in 1.0 L of preheated (60 °C), demineralized water. The addition of HNO₃ to the metal nitrate solution was required to keep the pH constant at 7 ± 0.05 during the precipitation process due to the basicity of the silicate solution. During the precipitation

process, pH was controlled through the flows of the nitrate and silicate solutions, and the temperature was maintained at 60 °C. At the end of the precipitation process, the precipitate was aged at 60 °C for 1 h (with continuous stirring). During this hour, the pH value was maintained at 7 \pm 0.02 by addition of the remaining metal solution. Then, the precipitate was aged at room temperature overnight. Afterwards, the precipitate was filtered and washed three times with demineralized water, followed by drying overnight at 110 °C. The sample was then calcined at 300 °C in a flow of N₂ for 4 h (heating rate 2 °C min⁻¹). This sample was denoted as Cu–Ni/SiO₂–Copr.

Deposition-coprecipitation. An aqueous solution of metal nitrates [(Cu(NO₃)₂·3H₂O (0.0690 M), and Ni(NO₃)₂·6H₂O (0.0345 M), 250 ml] was coprecipitated using a solution of Na₂CO₃ (Sigma-Aldrich, 500 ml, 0.103 M) in 1.0 L of preheated (60 °C), demineralised water containing a suspension of SiO₂ (207 m² g⁻¹, in a size range of 150–300 μ m). During the precipitation process, pH was maintained at 7 ± 0.05 by controlling the flows of the nitrate and carbonate solutions, and the temperature was maintained at 60 °C. At the end of the precipitation process, the precipitate was aged at 60 °C for 1 h (with continuous stirring). During this hour, the pH value was maintained at 7 \pm 0.02 by the addition of the remaining metal solution. The precipitate was then aged at room temperature overnight. Afterwards, the precipitate was filtered and washed three times with demineralized water, followed by drying overnight at 110 °C. The sample was then calcined at 300 °C in a flow of N2 for 4 h (heating rate 2 °C min⁻¹). This sample was denoted as Cu-Ni/SiO₂-Dep-Copr.

2.2 Characterization

The chemical composition of both fresh and spent (tested in high pressure CO hydrogenation) samples was determined by an ICP-OES (Perkin-Elmer, model Optima 7300) using Ar as plasmogene. In a typical analysis, 5 g of $K_2S_2O_7$ was melted together with 0.25 g sample and dissolved in 10 ml HCl in 200 ml water and then analyzed.

The BET surface area was determined by N₂-adsorption at 77 K by means of a QuantaChrome Autosorb iQ₂ gas sorption analyzer. The specific surface area was analyzed using a 7-point, linear BET plot in the range of $p/p_0 = 0.05$ -0.3. Prior to the BET measurement, the sample was dried under nitrogen flow (200 Nml min⁻¹) at 150 °C for 2 h.

In order to understand the reduction and calcination processes of the nitrate sample precursor (Cu–Ni/SiO₂–IWI), TGA was carried out with a NETZSCH STA-449-F1 thermoanalyzer. First, 15 mg of the sample was loaded into an alumina sample holder. The sample was then heated to 400 °C in a 120 ml min⁻¹ flow of 4.2 mol% H₂/N₂ (for reduction) or pure N₂ (for calcination) with a heating rate of 2 °C min⁻¹.

In situ XRD was performed with a PANalytical X'Pert PRO diffractometer equipped with an Anton Paar XRK 900 *in situ* cell and a gas flow control system for H₂-TPR. Silica supported Cu–Ni samples were heated in flowing 2 mol% H₂/He up to 300 °C for 1 h (heating rate 20 °C min⁻¹ below 160 °C and

1 °C min⁻¹ above 160 °C). Each XRD measurement took 10 minutes, and the temperature was maintained during the XRD measurement. After reduction, the sample was cooled to room temperature, and then a long XRD scan (640 minutes) was performed in order to estimate the particle size of the formed metallic phase. An estimate of the average particle diameter ($d_{p,XRD}$) was obtained from diffraction peak broadening by means of the Scherrer equation:⁴⁸

$$d_{\rm p,XRD} = \frac{0.9\lambda}{\beta_{\rm 1/2} \cos(\theta)}$$

Here λ is the X-ray wavelength, θ is the Bragg angle, and $\beta_{1/2}$ is the full width at half maximum of the diffraction peak corrected for instrumental broadening (using a highly crystal-line Si standard).

TEM images were acquired using an FEI Titan 80-300 aberration corrected microscope operated at 300 kV and an FEI Tecnai T20G2S microscope operated at 200 kV. The samples were dispersed in dry form on the TEM grids, which were Au-grids coated with a holey carbon film.

2.3 CO hydrogenation

CO hydrogenation experiments were performed in a high pressure, fixed-bed flow reactor setup. Detailed descriptions of the experimental setup and the experimental procedure have been provided in ref. 49-52. The catalyst is located in a guartz tube within a stainless steel pressure shell. As the inside of the quartz tube is pressurized, the pressure shell is also pressurized with nitrogen to ensure that no pressure gradient exists across the quartz tube wall. High pressure CO hydrogenation was carried out at P = 100 bar, T = 275 °C, GHSV = 4000 h⁻¹ (based on total bed volume and gas flow referring to 298.15 K and 1 bar), feed: $H_2/CO = 2$ (vol/vol). The temperature was measured in a steel thermo pocket touching the external surface of the quartz tube. The product was analyzed by using an online gas chromatograph equipped with flame ionization and thermal conductivity detectors (6890N GC-FID/TCD from Agilent Technologies). The characterized oxygenates were: DME, methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1propanol and ethyl acetate. Additionally, methane, ethane, ethene, propane, CO, CO2 and H2 were analyzed. A bubble flow meter was used for determining the volumetric flow rate of the reactor effluent. Prior to the reaction, all catalyst precursors were reduced in situ at atmospheric pressure by a flow of 1.4 mol% H₂ in N₂ for 12-14 h at 280 °C (which was reached using a heating rate of 1 °C min⁻¹). The carbon mass balance was generally fulfilled to within 5 mol%. The conversion of CO $(X_{\rm CO})$ is calculated from the molar flow rates of CO $(F_{\rm CO})$ into and out of the reactor:

$$X_{\rm CO} = \frac{F_{\rm CO}^{\rm in} - F_{\rm CO}^{\rm out}}{F_{\rm CO}^{\rm in}} \cdot 100\%$$

The selectivity to a given product (S_i) is based on the total number of carbon atoms in the characterized products:

$$S_i = \frac{n_i y_i}{\sum n_i y_i} \cdot 100\%$$

Here $n_i (n_i \ge 1)$ is the number of carbon atoms in component i, and y_i is the mole fraction of component i in the product. The space time yield (STY_{MeOH}) of methanol is the production rate of methanol per mass of catalyst:

$$\mathrm{STY}_{\mathrm{MeOH}} = \frac{M_{\mathrm{MeOH}} F_{\mathrm{MeOH}}}{m_{\mathrm{cat}}} \left[\mathrm{kg} \mathrm{kg}_{\mathrm{cat}}^{-1} \mathrm{h}^{-1} \right]$$

Here, M_{MeOH} is the molar mass of methanol and F_{MeOH} is the molar flow rate of methanol out of the reactor. We report the STY in the units of mass of methanol produced per hour and per mass of catalyst (m_{cat}), which includes both active metals and support.

3. Results and discussion

3.1. Catalyst structure

3.1.1 ICP-OES elemental analyses and BET surface area studies. The ICP-OES elemental analysis results for all fresh samples are listed in Table 1. The desired composition was 20 wt% Cu + Ni metal loading on silica, and the samples are close to this value. In addition, the Cu/Ni atomic ratios are also close to the expected atomic ratio of Cu/Ni = 2. Compared to the original SiO₂ support (207 m² g⁻¹) the specific surface area of the impregnated sample (Cu-Ni/SiO₂-IWI) has decreased about 44% to 116 m² g⁻¹. This is presumably due to blocking of the pore structure by the loaded metals. Using the same silica, the surface area of the depositioncoprecipitation sample, Cu-Ni/SiO2-Dep-Copr, increases to 253 m² g⁻¹. The increase in the surface area can presumably be ascribed to the presence of small precipitated nanoparticles in the sample. The coprecipitated sample, Cu-Ni/SiO₂-Copr, shows the highest specific surface area of 322 m² g⁻¹. This approach to co-precipitate the SiO₂ from Na₂SiO₃ together with metal precursors seems to be an efficient way to prepare high surface area silica supported catalysts. The specific surface areas of the three samples prepared by different methods are in increasing order: impregnation < depositioncoprecipitation < coprecipitation.

3.1.2 *In situ* XRD and TGA studies. The diffraction patterns marked "im" in Fig. 1 are the XRD patterns at selected temperatures during *in situ* reduction of the Cu–Ni/SiO₂–IWI precursor in a flow of 2 mol% H₂/He. The catalyst precursor contains Cu/Ni hydroxynitrates that are formed during the drying of impregnated metal nitrate precursors at elevated temperature (100 °C), which results in agglomeration during hydrolysis of metal nitrate hydrate to metal hydroxynitrate.^{53,54} There are no observed reflections of either CuO or NiO in the XRD patterns during the reduction process. The main reduction occurs between 230 °C and 240 °C. Metallic Cu and Ni have two main reflections, belonging to the [111] and the [002] crystal planes, at 43.3° and 50.4° for Cu and at 44.5° and 51.8°

Table 1 ICP-OES elemental analysis and BET surface area measurement results of fresh samples

Catalysts	Analyzed loading (wt%)			Metal loading in reduced catalyst ^a	Cu/Ni (atomic ratio)		BET surface area	
	Cu Ni Na Cu +		Cu + Ni (wt%)	Nominal	Measured	$m^2 g^{-1}$		
Cu–Ni/SiO ₂ –IWI	9.17	4.1	_	23.6	2.00	2.07	116	
Cu–Ni/SiO ₂ –Copr	13.0	5.30	0.027	22.0	2.00	2.26	322	
Cu-Ni/SiO ₂ -Dep-Copr	12.8	4.87	0.205	20.8	2.00	2.12	253	
				W -	$\vdash W$			

^{*a*} The metal loading in the reduced sample is calculated from the equation $W_{Cu+Ni} = \frac{W_{Cu} + W_{Ni}}{W_{Cu} + W_{Ni} + W_{SiO_2}} \cdot 100\%$ on the basis of the analyzed contents of Cu, Ni and Si.



Fig. 1 XRD patterns at selected temperatures during *in situ* reduction of the impregnated (im), deposition–coprecipitated (dc) and coprecipitated (cp) Cu–Ni/SiO₂ samples in a flow (100 ml min⁻¹) of 2 mol% H₂/He. Phase designations: \blacktriangle – Cu/Ni hydroxynitrate, \bullet – metallic Cu, and \blacksquare – Cu–Ni alloy.

for Ni (ICSD file 52265), respectively. In Fig. 1, the first reflection is located at 43.3° with a small shoulder at 43.7° and the second reflection is located at 50.4° with a shoulder at 50.7°. The reflections at 43.3° and 50.4° are assigned to a metallic Cu phase, and the shoulders located in between the metallic phases of Cu and Ni are assigned to Cu-Ni alloys. Based on ICP-OES analysis, the Cu/Ni molar ratio is 2.07. The Cu-Ni alloy phase composition calculated using Vegard's law is Cu/Ni = 2.0. From these analyses, about 4 mol% of isolated metallic Cu is estimated to exist in the reduced catalysts. It seems that the majority of Cu is alloyed with Ni, while a fraction of Cu is segregated from the alloy phase. It was reported that the standard reduction potential for Cu is 0.337 eV, which is higher than that of Ni (-0.25 eV).^{15,28} Cu is therefore more easily reduced than Ni, and reduced Cu can subsequently act as a catalyst to shift the reduction of Ni to lower temperature whereby the Cu-Ni alloys are formed. According to the Scherrer equation,⁴⁸ the average particle sizes are about 11 nm for Cu-Ni alloys and about 54 nm for Cu. In order to understand the reduction and calcination processes of nitrate precursors, TGA analyses were performed in inert gas (N2) flow and reducing gas (4.2 mol% H_2/N_2) flow. Fig. 2 shows the mass loss rate as a function of temperature in the two different gas atmospheres. In the flow of 4.2 mol% H_2/N_2 , there are three major mass loss peaks. The first peak starts at 210 °C and is centered at 250 °C, while the second and third peaks are centered at around 260 and 265 °C, respectively. In the flow of N₂, there is one major



Fig. 2 TGA analysis of the Cu–Ni/SiO₂–IWI sample in a flow (120 ml min⁻¹) of N₂ and 4.2 mol% H₂/N₂ respectively (heating rate 2 °C min⁻¹).

peak which begins at 210 °C and is centered at 250 °C. The calcination temperatures for Cu and Ni nitrates are reported to be between 210 and 280 °C.^{55–57} The first peak, centered at 250 °C, can therefore be ascribed to mass loss resulting from nitrate decomposition during calcination. The second peak centered around 260 °C in reducing gas flow is probably related to the beginning reduction of CuO, which is more easily reduced, and the reduced Cu then acts as a catalyst and enhances the reduction of Ni, whereby a double peak structure is seen in the mass loss curve. This might further indicate that Cu and Ni are not reduced simultaneously and that may be a part of the reason for the observed phase segregation.

The diffraction patterns marked "cp" in Fig. 1 show the in situ XRD scans on the Cu-Ni/SiO₂-Copr sample during the reduction process. No reflections of either CuO or NiO are observed in the XRD patterns in the as prepared oxide. Hence, these oxides are finely dispersed and in an X-ray invisible, amorphous form. The Cu-Ni alloy starts to emerge at 220 °C. Two symmetric reflections located at ~43.4° and at ~50.5° are observed after reduction. Interestingly, it seems that only the Cu-Ni alloy is formed in this case. According to the Scherrer equation,48 the particle size is about 4 nm for the Cu-Ni alloy phase. A very similar reduction process is observed for the Cu-Ni/SiO2-Dep-Copr sample in the in situ XRD studies (patterns marked "dc" in Fig. 1). Two symmetric reflections located at ~43.5° and at ~50.6° are observed after reduction, indicating the formation of a Cu-Ni alloy without the formation of a separate Cu phase. The particle size of the Cu-Ni alloy particles is estimated from XRD peak broadening to be 5 nm.

Long scan (640 minutes) XRD patterns at room temperature after reduction of silica supported Cu–Ni samples are shown in Fig. 3. The XRD particle size estimates of Cu–Ni alloys (based on the Scherrer equation⁴⁸), the fraction of metallic Cu in the reduced catalysts (for the impregnated catalyst) and the metal surface areas of all reduced samples are calculated and summarized in Table 2. The particle sizes of Cu–Ni alloys are 4 nm and 5 nm for catalysts prepared by coprecipitation and deposition–coprecipitation methods, respectively – significantly smaller than the particle size of the catalyst prepared *via* the impregnation method on SiO₂ (11 nm).

With respect to bulk Cu-Ni alloy formation, the phase diagram for the binary Cu-Ni bulk system shows phase segregation for a broad range of mixing ratios at room temperature^{24,25} and formation of a solid solution only above a certain critical temperature typically found in the 200-300 °C range depending on the alloy composition.²⁴⁻²⁷ In the case of Cu rich compositions, we have found in this study, as well as in a previous one,²⁹ that impregnated Cu-Ni samples form segregated phases of metallic Cu and Cu-Ni alloy. However, the present results for precipitated samples show that supported Cu-Ni in fact can form homogeneous alloys even when being rich in Cu. We have previously found that when the Cu-Ni alloys are rich in Cu, the particle size is larger than that for Ni-rich Cu-Ni alloys that show little or no segregation, and the particle size may thus also have an impact on the miscibility.²⁹ Some bimetallic systems such as Cu-Ru and Cu-Re are completely immiscible in the bulk.58,59 However, Cu-Ru and Cu-Re





do form bimetallic alloys when the particles are very small (on the order of 1.5 nm or smaller).³¹ It has been concluded that the behavior of small bimetallic clusters may be very different from that of substantially larger clusters.³¹ Using Monte Carlo simulations, Christensen et al.³⁰ suggested that this would also be the case for the Cu-Ni system, and the simulations indicated that particles up to a size of 1.9 nm would be alloved even at a temperature of absolute zero. This is because the energy cost in interface free energy upon formation of segregated particles counteracts the gain in free energy upon phase segregation.³⁰ Depending on the particle size and the temperature, the supported particles may therefore be alloved, even at temperatures where the bulk system is immiscible, and this can help to explain why the smaller particles in the precipitated samples appear to be fully alloyed, while the larger particles in the impregnated sample exhibit a segregation into Cu and Cu-Ni alloy.

3.1.3 TEM studies of the supported Cu-Ni catalyst precursors. Fig. 4 shows TEM images of the catalyst precursors prepared by the three different preparation methods as well as the corresponding particle size distributions. A clear difference in structure among these three catalyst precursors can be observed. For the impregnated catalyst (Cu-Ni/SiO₂-IWI), the particle size distribution is broad as shown in Fig. 4a and d. The observed particles span the range of 3 to 15 nm, and the average particle size is 8.5 nm. It was previously reported for silica-supported metal nitrates that the drying step is of vital importance for the particle size distribution.53,54 Drying at elevated temperature (90 °C) resulted in agglomeration of metal hydroxynitrate particles.^{53,54} This could help to explain the rather broad particle size distribution observed for the impregnated catalyst in the present study. It has previously been reported that drying at ambient temperatures could prevent the formation of large metal hydroxynitrate crystals, but the subsequent calcination step still resulted in broad particle size distributions.⁶⁰

For both the deposition–coprecipitation prepared catalyst $(Cu-Ni/SiO_2-Dep-Copr)$ and the catalyst prepared using coprecipitation $(Cu-Ni/SiO_2-Copr)$, the particle sizes are distributed in a narrow range, and most of the particles are in the size range between 3 and 5 nm. The average particle sizes are 4.3 nm and 4.1 nm for the Cu-Ni/SiO_2-Dep-Copr and Cu-Ni/SiO_2-Copr catalysts, respectively. A comparison of the size of the metal precursor particles from TEM (Fig. 4) to the metal particle size determined by *in situ* XRD (Table 2) shows that the particle sizes of the metal precursors in the

 Table 2
 XRD particle size estimates for Cu-Ni alloys, the fraction of metallic Cu in the reduced catalysts and estimated metal surface areas of all reduced samples

Catalysts	$d_{\mathrm{p,XRD}}^{a}$ [nm]	Fraction of metallic Cu^b [mol%]	Mass of metal ^{c} [g g _{cat} ⁻¹]	$S_{\text{metal}}^{d} [\text{m}^2 \text{g}_{\text{cat}}^{-1}]$
CuNi/SiO ₂ -IWI	11	4	17.1	10.4
CuNi/SiO ₂ -C	4	0	17.7	29.4
CuNi/SiO ₂ -DC	5	0	18.3	24.4

^{*a*} XRD particle size estimate for Cu–Ni alloys. ^{*b*} Calculated from Vegard's law and ICP-OES results. ^{*c*} Active metal is metallic Cu + Ni, the weight of metal material per gram of catalyst precursor, which is determined using ICP-OES analysis. ^{*d*} Metal surface area calculated from the alloy particle size and the metal content.



Fig. 4 TEM images of (a) Cu-Ni/SiO₂-IWI (Cu and Ni present as the nitrates), (b) Cu-Ni/SiO₂-Dep-Copr (Cu and Ni present as the oxides), and (c) Cu-Ni/SiO₂-Copr (Cu and Ni present as the oxides) and particle size distributions of (d) Cu-Ni/SiO₂-IWI, (e) Cu-Ni/SiO₂-Dep-Copr, and (f) Cu-Ni/SiO₂-Copr precursor samples.

as-prepared samples are very similar to the corresponding reduced alloy particles. Thus, there does not appear to be discernible sintering during the reduction process, except for the impregnated sample where the reduction leads to large isolated Cu particles (54 nm) in addition to the alloy particles.

3.2 CO hydrogenation

The steady state performance in CO hydrogenation of silica supported Cu–Ni catalysts prepared by different methods is shown in Table 3. The major product is methanol with a selectivity above 99 mol% in all cases, while the rest of the product consists of a small amount of oxygenates (ethanol and/or DME) and methane. The space time yield of methanol is 2 to 3 times higher for the coprecipitated and depositioncoprecipitated catalysts (0.52 and 0.66 kg kg_{cat}⁻¹ h⁻¹, respectively) than for the impregnated catalyst (0.19 kg kg_{cat}⁻¹ h⁻¹). This is most likely due to the differences in the metal particle sizes (see Table 2). The high selectivity towards methanol over Cu–Ni catalysts is in agreement with our previous results on CuNi (1/1 molar ratio) alloys⁴³ and with other studies.^{20,23,41,42,44,61}

However, a significant amount (53-82 wt%) of Ni has been lost after the CO hydrogenation test (Table 4), which is ascribed to loss by volatile nickel carbonyl formation similar to what is known from pure Ni.⁴⁵⁻⁴⁷ The loss of Ni means that there is a variable Ni-content in the catalyst during the test. It is interesting to note that the selectivity and activity in MeOH synthesis have been very stable during even prolonged tests. Fig. 5 shows the development of space time yield (STY) and selectivity to methanol as functions of time on stream for the Cu-Ni/SiO₂-Dep-Copr catalyst. The methanol STY increases from 0.46 to 0.66 kg kg_{cat}⁻¹ h⁻¹ during the first 10 h and then stabilizes. In our previous paper, we have found a similar activation process over the silica supported CuNi catalysts as well.43 The activation process could be related to introduction of syngas (flushing the reactor volume), surface segregation effects and Ni loss from Cu-Ni alloys. The catalyst precursor is first reduced in H₂/N₂ gas flow, and then exposed to the more reducing CO and H_2 mixture. After reduction in H_2/N_2 , Cu presumably occupies the first surface layer due to its lower surface energy, whereas under reaction conditions, Ni may move to the surface due to the stronger bonding of CO to Ni than to Cu.43,62,63 In our previous work, we proposed that Ni is pulled out to the surface of the alloy particles and forms a bimetallic Cu-Ni surface.43 However, the present results suggest that Ni not only segregates to the surface but is even being leached from the surface of the particles very quickly due to the high CO partial pressure. After a short initial phase, diffusion of Ni to the surface presumably becomes rate controlling for the Ni removal. We therefore in the end effectively operate with an essentially pure Cu surface for CO hydrogenation. It is of interest to note that other researchers have tested Cu-Ni alloys in CO hydrogenation at high CO partial pressure conditions. For example, Fraga et al.44 tested CO hydrogenation over Cu-Ni/Al₂O₃ catalysts and noted a change in product yields from hydrocarbons and higher alcohols towards MeOH over about 10 hours of operation. The reason was not explained by the authors, but may be rationalized in the light of our observations of changes in the alloy composition. When the catalyst contains Ni, it produces hydrocarbons and

Table 3Results for CO hydrogenation at steady state over silica supported Cu-Ni catalysts prepared by different methods. Experimentalconditions: P = 100 bar, $T = 275 \,^{\circ}$ C, GHSV = 4000 h⁻¹ and H₂/CO = 2.0 vol/vol

Sample	TOS ^a	$X_{\rm CO}^{\ \ b}$	Carbon base	Carbon based selectivity (CO ₂ -free) [mol%]				
	[h]	[%]	MeOH	Ethanol	Methane	DME	$[\text{kg kg}_{\text{cat}}^{-1} \text{h}^{-1}]$	
Cu-Ni/SiO ₂ -IWI	42	8.5	99.7	0.2	0.1	0	0.19	
Cu-Ni/SiO ₂ -Copr	28	14.3	99.1	0.2	0.6	0.1	0.52	
Cu-Ni/SiO ₂ -Dep-Copr	26	16.6	99.2	0.3	0.2	0.1	0.66	

^a TOS: time on stream. ^b CO conversion.

Table 4 ICP-OES analysis of both fresh and spent Cu-Ni catalysts

Sample	TOS ^a [h]	Fresh catalyst [wt%]			Spent catalyst [wt%]				Ni	
		Cu	Ni	Si	Ni loading ^b	Cu	Ni	Si	Ni loading ^b	loss ^c [%]
Cu-Ni/SiO ₂ -IWI	166	9.17	4.1	20	7.3	11.0	1.26	35.5	1.4	82
Cu-Ni/SiO ₂ -Copr	28	13.0	5.30	30.4	6.4	12.4	1.95	33.8	2.2	65
Cu-Ni/SiO ₂ -Dep-Copr	26	12.8	4.87	34.4	5.3	13.0	2.20	33.5	2.5	53
							C 1	11/		

^{*a*} TOS: time on stream. ^{*b*} The Ni loading in the reduced catalyst is calculated from the equation $W_{\text{Ni}} \frac{\text{fresh}}{\text{spent}} = \frac{W_{\text{Ni}}}{W_{\text{Cu}} + W_{\text{Ni}} + W_{\text{SiO}_2}} \cdot 100\%$. ^{*c*} Ni loss is





Fig. 5 Space time yield and selectivity of methanol as functions of time on stream for the Cu-Ni/SiO₂-Dep-Copr catalyst. The operating conditions are: P = 100 bar, T = 275 °C, GHSV = 4000 h⁻¹ (based on total bed volume and gas flow referring to 298.15 K and 1 bar), feed: H₂/CO = 2 (vol/vol).

higher alcohols, but as the composition shifts towards pure Cu, the catalyst changes to produce mainly methanol. A very recent study by Xiao *et al.*²³ made similar observations without mentioning that Ni was lost from the catalyst. Their XRD data on CuNi₃ catalysts (Cu/Ni = 1/3, molar ratio) clearly showed that the freshly reduced catalyst consisted of a Cu–Ni alloy, but after the CO hydrogenation test, the XRD reflections had shifted towards the position for metallic Cu.²³

For pure metallic Ni, it is well established that the thermodynamics may favor formation of volatile Ni(CO)₄ under some conditions. For example, when the partial pressure of CO is higher than 0.2 bar and the temperature is lower than 425 °C, carbonyl formation will take place and removal of nickel from the catalytic reactor occurs.⁴⁶ According to thermodynamic calculations, Shen et al.⁴⁶ reported that conditions for which the equilibrium Ni(CO)₄ pressure is less than *ca.* 1×10^{-11} bar result in stable methanation activity. Conversely, much higher partial pressures of Ni(CO)₄ will lead to the transport of nickel through the catalyst bed and ultimately to the removal of nickel from the reactor.⁴⁶ It is therefore not surprising that Ni was lost in our high CO pressure tests on Cu-Ni catalysts as well as in the mentioned examples from the literature. For example, at a starting CO pressure of 50 bar, the equilibrium Ni(CO)₄ pressure is very high (about 1 to 5 bar in the 250–300 °C range) - significantly higher than the upper limit for stable operation given by Shen et al.46 It should be noticed that Ni is not only often used as an alloying component with Cu for high pressure CO hydrogenation, but also used as a promoter for high pressure CO hydrogenation to higher alcohols in other catalyst systems.^{64–69} The present results show that loss of Ni by carbonyl formation is not only a problem for pure Ni catalysts, but also something that must be considered when Ni-containing alloy catalysts are used under conditions with elevated partial pressure of CO.

4 Conclusion

Silica supported, bimetallic Cu-Ni (20 wt% Cu + Ni on silica, Cu/Ni = 2, molar ratio) alloy catalysts have been prepared via incipient wetness impregnation, coprecipitation, and depositioncoprecipitation methods and tested for CO hydrogenation. The approach to co-precipitate the SiO₂ from Na₂SiO₃ together with metal precursors seems to be an efficient way to prepare high surface area silica supported catalysts with small Cu-Ni particles (BET surface area up to 322 m² g⁻¹, and metal area calculated from XRD particle size up to 29 m² g⁻¹). TEM studies on as-prepared catalyst precursors show that both the deposition-coprecipitation and coprecipitation methods yield small, homogeneous particles in the size range between 3 and 5 nm, while catalyst preparation by impregnation yields larger particles (8.5 nm). The particle sizes of the metal precursors in the asprepared samples are similar to the corresponding reduced alloy particles, and there does thus not appear to be discernible sintering during the reduction process. An exception is the impregnated sample where the reduction leads to large isolated Cu particles (54 nm) in addition to Cu-Ni alloy particles. Monitoring of the crystal structure using XRD during in situ reduction shows that coprecipitation and deposition-coprecipitation methods are more efficient than the impregnation method for preparation of small and especially homogeneous Cu-Ni alloy nanoparticles. The small size of the metal particles in the precipitated samples is most likely the reason why homogeneous alloys are formed.

The supported Cu–Ni catalysts were tested in high pressure CO hydrogenation. The selectivity towards methanol was always higher than 99 mol%; however, analyses of spent catalysts show that serious Ni loss by carbonyl formation occurs for the Cu–Ni alloy catalysts during high pressure CO hydrogenation. Due to the strong bonding of CO to Ni, it seems quite possible that loss of Ni by carbonyl formation will also take place for other Ni containing alloys if these are used under conditions with high partial pressures of CO. Our observations can help to explain observations of transient behavior in the selectivity during CO hydrogenation previously left unexplained in the literature.

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