Surface Segregation in CuNi Nanoparticle Catalysts During CO₂ Hydrogenation: The Role of CO in the Reactant Mixture

Ioannis Zegkinoglou,† Lukas Pielsticker,‡ Zhong-Kang Han,§ Nuria J. Divins, † David Kordus,† Yen-Ting Chen,§ Carlos Escudero,§ Virginia Pérez-Dieste, § Beien Zhu,† Yi Gao,§ and Beatriz Roldan Cuenya,†∥

†Department of Physics, Ruhr University Bochum, 44780 Bochum, Germany
‡Division of Interfacial Water and Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China
§ALBA Synchrotron Light Source, Carrer de la Llum 2-26, Cerdanyola del Vallès, 08290 Barcelona, Spain
∥Department of Interface Science, Fritz-Haber Institute of the Max Planck Society, Berlin 14195, Germany

ABSTRACT: Surface segregation and restructuring in size-selected CuNi nanoparticles were investigated via near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) at various temperatures in different gas environments. Particularly in focus were structural and morphological changes occurring under CO₂ hydrogenation conditions in the presence of carbon monoxide (CO) in the reactant gas mixture. Nickel surface segregation was observed when only CO was present as adsorbate. The segregation trend is inverted in a reaction gas mixture consisting of CO₂, H₂, and CO, resulting in an increase of copper concentration on the surface. Density functional theory calculations attributed the inversion of the segregation trend to the formation of a stable intermediate on the nanocatalyst surface (CH₃O) in the CO-containing reactant mixture, which modifies the nickel segregation energy, thus driving copper to the surface. The promoting role of CO for the synthesis of methanol was demonstrated by catalytic characterization measurements of silica-supported CuNi NPs in a fixed-bed reactor, revealing high methanol selectivity (over 85%) at moderate pressures (20 bar). The results underline the important role of intermediate reaction species in determining the surface composition of bimetallic nanocatalysts and help understand the effect of CO cofeed on the properties of CO₂ hydrogenation catalysts.

INTRODUCTION

Methanol is industrially produced from the conversion of a synthesis gas mixture consisting of CO₂, CO, and H₂ over Cu/ZnO/Al₂O₃ catalysts at moderate temperatures (230–280 °C) and high pressures (50–120 bar). Cu(211) step edges associated with bulk defects, such as stacking faults and twin boundaries terminating at the surface, in combination with nearby Zn atoms acting as adsorption sites for oxygen-bound intermediates, have been shown to be catalytically active in this system.¹ Despite its wide use, the Cu/ZnO/Al₂O₃ catalytic system is not free of drawbacks, including low stability due to sintering and the need for high pressures (at least 50 bar). Several studies have shown that doping of Cu catalysts with Ni drastically increases the rate of methanol production from CO₂ + CO + H₂ mixtures,²−⁷ whereas such a promoting effect is not observed in reactant mixtures only consisting of CO₂ and H₂.² Although ¹⁴C-labeling experiments have demonstrated that CO₂ is the main source of carbon for methanol synthesis over Cu in CO₂ + CO + H₂,⁸,⁹ the presence of Ni on the surface of the catalyst is believed to be beneficial, possibly because of the stabilization of CO species, which are then hydrogenated to methanol.⁹ It has been suggested that the role of CO in the reactant mixture is solely that of a promoter, inducing surface segregation of Ni, to which CO can then bind.⁷,¹⁰ While in situ infrared spectroscopic studies of CuNi catalysts performed in pure CO have indeed indicated surface segregation of Ni in the exclusive presence of CO,¹¹ such information has not been reported to date for the catalytic reaction conditions.

Here we report the results of a phase segregation study of CuNi bimetallic nanoparticles (NPs) supported on SiO₂/Si(111) under CO₂ hydrogenation conditions in a gas mixture consisting of CO₂ + CO + H₂. Using near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), we observed Ni surface segregation in pure CO, but Cu segregation in the CO₂ + CO + H₂ reactant mixture. Density functional theory (DFT) calculations indicate that the formation of a stable intermediate species (CH₃O) is responsible for the inversion of the segregation trend. These results show that the role of CO in

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the reactant mixture needs to be reconsidered and that intermediate reaction products might be key in determining the structure and surface composition of bimetallic catalysts and their catalytic behavior through surface segregation phenomena. Finally, we demonstrate that our CuNi NPs supported on SiO₂ are promising methanol synthesis catalysts due to their high selectivity (>85%) at moderate pressure (20 bar).

**EXPERIMENTAL SECTION**

Size-selected bimetallic Cu₀.₅Ni₀.₅ NPs with an average diameter of 5 nm were synthesized via inverse micelle encapsulation in a toluene solution using poly(styrene)-block-poly(2-vinylpyridine) (PS-P2VP) diblock copolymers (PS:P2VP ratio of 48500:70000, Polymer Source, Inc.) for the formation of the micellar cages, and copper(II) nitrate hexahydrate (Cu(NO₃)₂·6H₂O) and nickel(II) nitrate trihydrate (Ni(NO₃)₂·3 H₂O) as metal salts. Details of the synthesis procedure have been reported elsewhere. The particles were deposited on SiO₂/Si(111) substrates via dip-coating (at a speed of 5 cm/min), and the polymeric ligands were subsequently removed by an O₂ plasma treatment (SPI Plasma Prep III Plasma Etcher, 20 min, 20 W, 0.5 mbar).

In order to test the catalytic reactivity of the CuNi NPs under realistic reaction conditions, powder catalyst samples consisting of NPs from the same synthesis solution as above, but supported on nanocrystalline silica (12 nm, Strem Chemicals, Inc., 5% nominal weight loading), were prepared by incipient wetness impregnation and subsequent calcination. Thermogravimetric analysis (TGA) in synthetic air (20% O₂, 5% nominal weight loading), were prepared in a stainless steel ow reactor with inner glass coating. A 60 mg portion of the catalyst was mixed with 240 mg of SiC powder (46 grit, Alfa Aesar) and loaded between two quartz wool plugs. The catalyst was calcined in synthetic air with a flow rate of 50 mL/min in a furnace oven (Heraeus ROF 4/50) at 400 °C for 4 h to remove the polymeric carbon from the inverse micelle encapsulation synthesis. The actual metal loading of the SiO₂-supported catalysts was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The results of the ICP-OES measurements are shown in Table S1 in the SI, where additional details on the characterization of the catalyst samples are also provided.

The morphology of the SiO₂/Si(111)-supported NP samples was investigated with atomic force microscopy (AFM) in the initial, as-prepared state (after the ex situ O₂ plasma treatment) and after the NAP-XPS studies. The AFM images were acquired in tapping mode (Bruker MultiMode 8). The size distribution of the NPs was determined using the open-source software Gwyddion, based on the particle heights extracted from the AFM images. The morphology of the silica-supported powder catalyst samples was investigated by scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) (JEM-2800, JEOL), both before and after the catalytic reaction.

NAP-XPS studies of the SiO₂/Si(111)-supported NPs were performed at the beamline CIRCE of the ALBA synchrotron in Barcelona (Spain). In order to obtain depth profile information on the elemental composition of the NPs, Cu 2p and Ni 2p spectra were acquired at two different photon energies: at 1160 eV, where the inelastic mean free path (IMFP) of the photoelectrons in Cu and Ni is approximately 0.6 nm, and at 1540 eV, where the IMFP is approximately 1.1 nm. Detailed values for the IMFPs are given in Table S2 (SI). Measurements were performed consecutively in O₂ (0.4 mbar, 400 °C); in H₂ (0.4 mbar, 400 °C); in a reaction mixture consisting of CO (vol 11.5%), CO₂ (4.5%), and H₂ (84%) (total pressure: 0.48 mbar; 210 and 270 °C); again in O₂ (0.4 mbar, 400 °C); and in pure CO (0.4 mbar, 270 °C). The heating ramp rate was 20 °C/min and the duration of the measurements about 3 h per temperature point. During the initial annealing in O₂ all adventitious carbon species (due to sample transfer in air) are removed from the sample surface prior to the acquisition of the spectra, as confirmed by high-resolution C 1s scans (see Figure S2, Supporting Information). After each annealing step, the sample was cooled down in the gas, the chamber was evacuated, and the new gas (or gas mixture) was introduced at room temperature. The energy calibration in all XPS spectra was performed using the elemental Si 2p₃/₂ peak of the SiO₂/Si support at a binding energy of 99.4 eV as reference. The Cu 2p₃/₂ and Ni 2p₃/₂ regions were fitted with Gaussian–Lorentzian line shapes (ratio 0.3) and a linear background. For details of the fitting procedure, the reader is referred to the SI, as well as to ref 14.

In order to extract the segregation energies, spin-polarized DFT calculations were performed using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) implemented in the VASP code. The valence electronic states were expanded in the basis of plane waves with the core–valence interaction represented using the projector augmented wave (PAW) approach and a cutoff of 400 eV. For the calculation of the adsorption energies of the various gas molecules on the surface of the catalyst, the lateral interactions between the molecules were taken into consideration. The compounds which are more stable and more strongly adsorbed on the surface are those which mostly affect the surface segregation trend. Further information on the calculations is given in the SI.

The catalytic activity measurements of the SiO₂-supported powder catalyst were performed in a stainless steel fixed-bed ow reactor with inner glass coating. A 60 mg portion of the catalyst was mixed with 240 mg of SiC powder (46 grit, Alfa Aesar) and loaded between two quartz wool plugs. The catalyst was reduced in a H₂ + He mixture (vol 20:80) at 400 °C for 1.5 h and a flow rate of 50 mL/min. Afterward, the sample was cooled down to 210 °C, and the reactor was purged with He. Two different reaction mixtures were used for the catalytic tests (TG1, CO:CO₂:H₂ = 10:4:72, balanced in He, and TG2, CO₂:H₂ = 22:66, also balanced in He) using a total ow rate of 12 mL/min. A 60 mg portion of fresh catalyst from the same batch was used for each test. Two different batches were used to confirm the reproducibility of the results. Helium was used as an internal standard. The catalytic tests were performed consecutively at 1 bar and at 20 bar, at three different reaction temperatures (210, 240, 270 °C). The reaction products were analyzed online by a 7890B gas chromatograph (GC; Agilent Technologies, Inc.) equipped with two thermal conductivity detectors (TCD) and a flame ionizing detector (FID). All data points were acquired after a steady state was reached and are an average of at least five consecutive injections in the GC.

**RESULTS AND DISCUSSION**

Representative AFM images of Cu₀.₅Ni₀.₅ NPs supported on SiO₂/Si(111) acquired before and after the NAP-XPS measurements are shown in Figure 1. The corresponding size distribution histograms are shown in Figure S3 (SI). It is...
evident that the NPs do not undergo any significant morphological change during the NAP-XPS measurements. The average NP height and interparticle distance remain unaffected under NAP-XPS conditions, with no indication of sintering. This is at least partially assigned to the initial ex situ O2 plasma treatment prior to the catalytic reaction that leads to the stabilization of the NPs on the substrate. Morphological characterization of the SiO2-supported powder catalyst, performed by STEM/EDS before and after the catalytic reaction (Figure 2), confirms their bimetallic nature and the elemental composition of the NPs, as well as the absence of drastic agglomeration. An increase of the average NP size (up to 8 nm in some cases) was however observed after the reaction at 20 bar. Some local variations of the Cu: Ni metal ratio were observed from NP to NP in some cases, but the bimetallic nature of the NPs and the average elemental composition of Cu0.5Ni0.5 were confirmed in all investigated samples.

NAP-XPS spectra of the Cu 2p3/2 and Ni 2p3/2 core level regions acquired under different environmental conditions at two photon energies (1160 and 1540 eV) are shown in Figure 3.

Upon annealing in O2 (0.4 mbar) at 400 °C, both metals are highly oxidized. Cu is present in the form of Cu2+ species, while the oxidation state of Ni is mostly Ni3+ (binding energy 856.8 eV), with only about 5% of NiO (855.1 eV) present. The presence of Ni(OH)2 or NiO(OH) cannot be ruled out because the binding energy of these species is too close to that of Ni2O3 for a definite assignment. However, given that no source of hydrogen or water was present in the XPS chamber during the initial O2 annealing, and in accordance with our previous studies of CuNi catalysts, we tentatively attribute the peak at 856.8 eV to Ni2O3. Such species are unstable in bulk materials but have been reported for thin films and nanostructures. They are created during the initial O2 plasma treatment and have been shown to play an important role in determining the segregation trend in CuNi catalysts. Another possibility that cannot be excluded is that the peak at 856.8 eV is due to Ni2+ species (NiO or mixed Cu$_{x}$Ni$_{1-x}$O), with a spectral contribution shifted to higher binding energies due to nanoconfinement effects.

Subsequent treatment in H2 (0.4 mbar, 400 °C) fully reduces both metals. The presence of Cu+ species cannot be excluded, because the binding energies of Cu0 and Cu+ differ by only ~0.1 eV, and Cu LMM Auger lines, which would help distinguish between the two, could not be observed in our experiment due to the low NP coverage in our samples. However, given that Ni is fully reduced in H2, it can be expected that Cu (which is more easily reduced) is mostly in its metallic state too. The oxidation state of the two metals remains unchanged under CO2 hydrogenation reaction conditions in the gas mixture consisting of CO2 + CO + H2 (0.48 mbar; 210 and 270 °C). Subsequent annealing in O2 (0.4 mbar, 400 °C) reoxidizes the metals (CuO, Ni3+/Ni(OH)2, small amounts of NiO), while dosing CO at 270 °C in the last step of the NAP-XPS sequence brings the metals back to their mostly metallic state, with only small amounts of Ni2O3 remaining. As expected, higher amounts of nickel oxides are observed in CO at the higher photon energy (12% Ni2O3 at

Figure 2. STEM images of a Cu0.5Ni0.5/SiO2 powder catalyst obtained (a) before the catalytic reaction, (b) after catalytic reaction in CO2 + H2 (vol. 1:3) and (c) after catalytic reaction in CO2 + CO + H2 (vol. 4.5:11.5:84%) at 20 bar (210—270 °C). EDS linear scans (d-f) show the relative amounts of Cu (red) and Ni (blue) along the lines shown in the respective STEM images in the upper row.
1540 eV) than at the surface-probing lower photon energy (9% Ni$_2$O$_3$ at 1160 eV), consistent with the fact that the reduction starts at the surface of the NPs and proceeds inward. The binding energies of the various Cu and Ni species, as determined from the fitting curves of the NAP-XPS spectra, are shown for the various environmental conditions in Figure S4 (SI).

The atomic percentages of the NPs at the two different probing depths were determined from the integrated intensities of the NAP-XPS peaks and summarized in Figure 4. After the initial O$_2$ annealing, the Ni:Cu atomic ratio is approximately equal to 60:40 at both photon energies. The fact that more Ni is probed in the near-surface volume of the NPs than what would be expected on the basis of the nominal atomic ratio indicates that surface segregation of Ni takes place when the NPs are fully oxidized. Subsequent reduction in H$_2$ results in a further increase of the amount of Ni directly at the surface (1160 eV) and a decrease deeper inside the NPs (1540 eV), while the opposite trend is observed for Cu. This indicates surface segregation of Ni in the presence of H$_2$.

Interestingly, the above trend is inverted upon heating in the reaction gas mixture consisting of CO$_2$ + CO + H$_2$ (vol 11.5:4:5:84). Already at a temperature of 210 °C, a significant increase of the Cu amount probed both at 1160 eV (increase from 37% to 53%) and at 1540 eV (increase from 45% to 53%) is observed, accompanied by a relative decrease of the Ni amount (from 63% to 47% at 1160 eV). These results clearly demonstrate surface segregation of Cu in the three-gas reaction mixture. At 270 °C, the Ni:Cu ratio on the surface slightly increases (to 55:45). Reoxidation of the NPs in O$_2$ after the reaction brings the particle composition back to its initial state, with Ni segregating again back to the surface (63% Ni at 1160 eV). The restructuring undergone by the NPs in the reactant mixture is thus fully reversible. The final step of the treatment sequence involves heating the sample in pure CO. As clearly shown in Figure 4, this induces strong Ni surface segregation, with a Ni:Cu ratio of 72:28 at 1160 eV (i.e., in the near-surface region) and 58:42 at 1540 eV (i.e., deeper into the NPs). The results of the NAP-XPS studies can be thus summarized as moderate surface segregation of Ni in O$_2$, stronger Ni surface segregation in H$_2$, and even stronger segregation in CO, with a remarkable inversion of this trend in a reaction mixture consisting of CO$_2$, CO, and H$_2$, which drives more Cu to the surface as compared to pure H$_2$ or CO, especially at the lower temperature (210 °C). A summary of the atomic percentages of the various metal species probed by NAP-XPS in all gaseous environments is given in Table S3 (SI).
The surface segregation of Cu observed in the CO-containing reaction mixture is surprising at first glance. Previous studies of the CuNi NPs have shown that annealing in a CO$_2$ + H$_2$ mixture (1:3 volume ratio) results in Ni surface segregation. Given that annealing in pure CO also drives Ni to the surface (Figure 4), one might have expected the same result for the CO$_2$ + CO + H$_2$ environment too. In order to understand the reason for the unexpected surface segregation of Cu in the latter gas mixture, we performed density functional theory (DFT) calculations in a model system consisting of a Ni-doped Cu crystal with a (211) crystallographic surface orientation. The (211) surface is an approximation of the step edges that compose the surface of large NPs, as is the case here. The segregation energy of a Ni solute atom in a Cu host lattice was calculated for various adsorbates (reactants, intermediate species, and final reaction products) at the surface of the system and for various Ni concentrations. The stability of the intermediate species was also calculated to provide an estimate of the relative significance of each adsorbate with respect to the determination of the segregation behavior. The calculated segregation energies along with the predicted segregation trends are shown in Table S4 (SI).

The segregation energy of Ni in a Cu host lattice with (211) surface is equal to $-0.06$ eV in O$_2$, $-0.2$ eV in H$_2$, and $-0.46$ eV in CO, indicating weak, moderate, and strong surface segregation of Ni, respectively, in these environments, in accordance with our NAP-XPS results. The calculations also indicate an energy value close to zero ($-0.01$ eV) for the segregation energy in a two-gas reactant mixture consisting of CO$_2$ and H$_2$. This is in accordance with previously reported NAP-XPS results which show that annealing in CO$_2$ + H$_2$ maintains the Ni surface segregation induced upon reduction in H$_2$. The Ni segregation energy calculated for the three-gas reaction mixture CO + CO + H$_2$ has a high negative value ($-0.88$ eV). This would mean stronger Ni surface segregation. The situation changes drastically, however, once the intermediate products formed during the main chemical reactions (methanation, methanol synthesis, reverse water gas shift reaction) are taken into consideration. These include HCOO, H$_2$COO, H$_2$COOH, H$_2$CO, H$_2$CO, and H$_2$COH. A reliable identification of such intermediates directly from C 1s XPS spectra is very challenging, due to the large number of carbonaceous species with the same or very similar binding energy around 285–286 eV (see Figure S5, SI). The (CH)$_n$ species are expected at binding energies around 284.7 eV and methoxy (CH$_3$O) species around 285.8 eV (see Table S5, Supporting Information). It is worth noting that the highest amount of carbonaceous adsorbates is measured under reaction conditions in CO$_2$ + CO + H$_2$ at 210 °C, i.e., under the conditions where the strongest Cu surface segregation was experimentally observed (Figure S6, Supporting Information). Nickel tetracarbonyls (Ni(CO)$_4$) are common volatile species known to form when Ni comes in contact with CO. The formation rate of these species is maximum at a temperature around 75–125 °C and drops sharply at higher temperatures. Although formation of carbonyl species while ramping up the sample temperature in the CO-containing reactant mixture or in pure CO in our measurements is possible, no indication of such adsorbates could be seen in our Ni 2p$_{3/2}$ XPS spectra at 210–270 °C in the binding energy region of 854.7–855.0 eV, where these would be expected. Furthermore, no change of the Ni to Si atomic ratio was observed under reaction conditions after the initial reduction (Figure S7, Supporting Information), which is additional evidence that no significant loss of Ni through volatile Ni(CO)$_4$ species occurred during the NAP-XPS measurements. The fact that the same observation, i.e., no significant loss of Ni, is also made in the ICP-OES measurements (see Table S1, Supporting Information) and in the STEM/EDS characterization (Figure 2) of the silica-supported powder catalyst after reaction at a much higher pressure (20 bar) further supports this conclusion. Even if low concentrations of such adsorbates are present under reaction conditions in NAP-XPS, they are not expected to affect the segregation trend significantly, as discussed below.

The calculations (Figures S8–S10, Supporting Information) showed that, compared with other species formed under reaction conditions, such as HCOO, CH$_3$O, and Ni(CO)$_4$, CH$_3$O is more stable, thus dominating the segregation behavior. The reaction of coadsorbed H and CO to form CH$_3$O is exothermic by about 0.16 eV. The reaction energy for gas phase CO, H$_2$, and CO$_2$ to form adsorbed CH$_3$O species is $-3.15$ eV, while the reaction energies to form HCOO and CH$_2$O are $-1.78$ and $-2.23$ eV, respectively. Accordingly, CH$_3$O is the main species formed in the CO$_2$ + CO + H$_2$ mixture. This species is thus expected to dominate the segregation behavior experimentally observed. Once CH$_3$O is formed on the surface of the catalyst, the segregation energy of Ni changes sign from negative ($-0.88$ eV) to positive (+0.22 eV), indicating inward segregation of Ni and surface segregation of Cu. This result provides a viable explanation for the inversion of the segregation trend in the CO$_2$ + CO + H$_2$ reaction mixture which is observed in our NAP-XPS studies compared to the CO-free mixture. The CH$_3$O species is only formed in the three-gas mixture, when both H$_2$ and CO are present. It is expected that increasing the reaction temperature from 210 to 270 °C accelerates the decomposition of the species (due to the higher entropy), thus limiting the Cu surface segregation trend. The Ni(CO)$_4$ species, if present, are not significant for the observed segregation behavior because they are very unstable: our stability calculations show that, after relaxation, Ni(CO)$_4$ changes to four CO molecules adsorbed on the surface. The fact that the experimentally observed segregation behavior (Figure 4) in the CO-containing reactant mixture is very different from that in pure CO (where a higher concentration of Ni(CO)$_4$ should be expected) further supports the conclusion that Ni carbonyls do not play a significant role in the segregation phenomena in our measurements under reaction conditions. It is noted that the HCOO species which are formed in the CO-free reactant mixture in principle also induces minimal surface segregation of Cu (segregation energy of 0.03 eV), but the lower stability of this species and the nearly zero segregation energy value mean that its presence is barely sufficient to invert the surface segregation of Ni observed in the CO$_2$ + H$_2$ mixture upon reduction in H$_2$. For the catalytic characterization of the silica-supported CuNi NPs in the fixed-bed reactor, the same reactant mixture and temperatures as in the NAP-XPS measurements, but higher pressures (1 and 20 bar versus 0.48 mbar for the NAP-XPS), were used. The catalyst was found to be highly selective toward methanol (86%) in CO$_2$ + CO + H$_2$ at 20 bar at a temperature of 210 °C (Figure 5a). The low-pressure and -temperature conditions under which such high selectivity is achieved make the catalyst an attractive alternative to the
Figure 5. (a) Selectivity toward methanol, methane, and C2/C3 products (ethane, propylene) during CO2 hydrogenation over the CuNi/SiO2 powder catalyst measured in a fixed-bed flow reactor in two different CO2 hydrogenation reactant mixtures (with and without CO) at two different pressures (1 and 20 bar). CO is not included as a product. (b) Production rate of methanol, methane, and C2/C3 products (ethane, propylene) during the catalytic testing of the CuNi/SiO2 catalyst. The normalization was based on the total metal (Cu + Ni) content (in milligrams) as determined by ICP-OES (Table S1, Supporting Information). The error bars, both in parts a and b, indicate standard deviation errors (repetition of characterization on fixed-bed experiments). The Journal of Physical Chemistry C

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identifying the adsorbate effect that will dominate the segregation trend during the reaction.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b09912. Details on XPS analysis, catalyst synthesis, and theoretical calculations; histograms of NP heights from AFM; binding energies and atomic ratios of metal species; calculated segregation energies from DFT; C 1s XPS spectra; structural and energetic information used in the DFT calculations; IMFP of photoelectrons; and ICP-OES results (PDF).

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: Roldan@fhi-berlin.mpg.de.*

### ORCID

Ioannis Zegkinoglou: 0000-0002-1101-6935
Carlos Escudero: 0000-0001-8716-9391
Beien Zhu: 0000-0002-0126-0854
Yi Gao: 0000-0001-6015-5694
Beatriz Roldan Cuenya: 0000-0002-8205-307X

### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Behrens, M.; Stoldt, F.; Kasatkin, I.; Kühl, S.; Hävecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Kniep, B. L.; et al. The Active Site of Methanol Synthesis over Cu/ZnO/Al2O3 Industrial Catalysts. Science 2012, 336, 893–897.
(2) Nerlov, J.; Chorkendorff, I. Methanol Synthesis from CO2, CO, and H2 over Cu(100) and Ni/Cu(100). J. Catal. 1999, 181, 271–279.
(3) Zhao, F.; Gong, M.; Zhang, Y.; Li, J. The Performance and Structural Study of CuNi Alloy Catalysts for Methanol Synthesis. J. Porous Mater. 2016, 23, 733–740.
(4) Zhao, F.; Gong, M.; Gao, K.; Zhang, Y.; Li, J.; Chen, R. Atomic Layer Deposition of Ni on Cu Nanoparticles for Methanol Synthesis from CO2 Hydrogenation. ChemCatChem 2017, 9, 3772–3778.
(5) Yang, Y.; White, M. G.; Liu, P. Theoretical Study of Methanol Synthesis from CO2 Hydrogenation on Metal-Doped Cu(111) Surfaces. J. Phys. Chem. C 2012, 116, 248–256.
(6) Stoldt, F.; Abild-Pedersen, F.; Wu, Q.; Jensen, A. D.; Temel, B.; Grunwaldt, J.-D.; Nørskov, J. K. CO Hydrogenation to Methanol on Cu–Ni Catalysts: Theory and Experiment. J. Catal. 2012, 293, 51–60.
(7) Vesselli, E.; Monachino, E.; Rizzi, M.; Furlan, S.; Duan, X.; Dri, C.; Peronio, A.; Africh, C.; Lacovig, P.; Balderschi, A.; et al. Steeiling the Chemistry of Carbon Oxides on a NiCu Catalyst. ACS Catal. 2013, 3, 1555–1559.
(8) Chinchenc, G. C.; Denny, P. J.; Parker, D. G.; Spencer, M. S.; Whan, D. A. Mechanism of Methanol Synthesis from CO2, CO/H2, and CO/H2O Mixtures over Copper/Zinc Oxide/Alumina Catalysts - Use of 14C-Labeled Reactants. Appl. Catal. B 1997, 30, 333–338.
(9) Yang, Y.; Mims, C. A.; Mei, D. H.; Peden, C. H. F.; Campbell, C. T. Mechanistic Studies of Methanol Synthesis over Cu from CO/CO2/H2O Mixtures: The Source of C in Methanol and the Role of Water. J. Catal. 2013, 298, 10–17.
(10) Nerlov, J.; Chorkendorff, I. Promotion through Gas Phase Induced Surface Methanol Synthesis from CO, CO2, and H2 over Ni/Cu(100). J. Catal. Lett. 1998, 54, 171–176.
(11) Yao, Y.; Goodman, D. W. In Situ IR Spectroscopic Studies of Ni Surface Segregation Induced by CO Adsorption on Cu-Ni/SiO2 Bimetallic Catalysts. Phys. Chem. Chem. Phys. 2014, 16, 3823–3829.
(12) Roldan Cuenya, B.; Beherafarid, F. Nanocatalysis: Size- and Shape-Dependent Chemisorption and Catalytic Reactivity. Surf. Sci. Rep. 2015, 70, 135–187.
(13) Pérez-Díeste, V.; Aballe, L.; Ferrer, S.; Nicolás, J.; Escudero, C.; Milán, A.; Pellegrin, E. Near Ambient Pressure XPS at ALBA. J. Phys.: Conf. Ser. 2013, 425, 072023.
(14) Pielsticker, L.; Zegkinoglou, I.; Divins, N. J.; Mistry, H.; Chen, Y.-T.; Kostka, A.; Borisboinik, J. A.; Roldan Cuenya, B. Segregation Phenomena in Size-Selected Bimetallic CuNi Nanoparticle Catalysts. J. Phys. Chem. B 2018, 122, 919–926.
(15) Blochl, P. E. Projector Augmented-Wave Method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953–17979.
(16) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169–11186.
(17) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. Comp. Mater. Sci. 1996, 6, 15–50.
(18) Wang, Z.; You, Y.; Yuan, J.; Yin, Y.-X.; Li, Y.-T.; Xin, S.; Zhang, D. Nickel-Doped La0.95Sr0.05Mn1+xNi3-xO8 Nanoparticles Containing Abundant Oxygen Vacancies as an Optimized Bifunctional Catalyst for Oxygen Cathode in Rechargeable Lithium–Air Batteries. ACS Appl. Mater. Interfaces 2016, 8, 6520–6528.
(19) Aggarwal, P. S.; Goswami, A. An Oxide of Tervalent Nickel. J. Phys. Chem. 1961, 65, 2105–2105.
(20) Kang, J.-K.; Rhee, S.-W. Chemical Vapor Deposition of Nickel Oxide Films from Ni(C2H5)2/O2. Thin Solid Films 2001, 391, 57–61.
(21) Zhang, X.; Liu, J.-X.; Zijlstra, B.; Pilot, J. A. W.; Zhou, Z.; Sun, S.; Hansen, J. E. J. Optimum Cu Nanoparticle Catalysts for CO2 Hydrogenation Towards Methanol. Nano Energy 2018, 43, 200–209.
(22) Wu, H. C.; Chang, Y. C.; Wu, J. H.; Lin, J. H.; Lin, I. K.; Chen, C. S. Methanation of CO and Reverse Water Gas Shift Reactions on Ni/SiO2 Catalysts: The Influence of Particle Size on Selectivity and Reaction Pathway. Catal. Sci. Technol. 2015, 5, 4154–4163.
(23) Liu, Y.-M.; Liu, J.-T.; Liu, S.-Z.; Li, J.; Gao, Z.-H.; Zuo, Z.-J.; Huang, W. Reaction Mechanisms of Methanol Synthesis from CO/CO2 Hydrogenation on CuO(111): Comparison with Cu(111). J. CO. Util. 2017, 20, 59–65.
(24) Mihaylov, M.; Hadjiivanov, K.; Knötzinger, H. Formation of Ni(CO)4 During the Interaction between CO and Silica-Supported Nickel Catalysts: An FTIR Spectroscopic Study. Catal. Lett. 2001, 76, 59–63.
(25) Shen, W. M.; Dumesic, J. A.; Hill, C. G. Criteria for Stable Ni Particle Size under Methanation Reaction Conditions: Nickel Transport and Particle Size Growth Via Nickel Carbylon. J. Catal. 1981, 68, 152–165.
(26) De Groot, P.; Coulon, M.; Dransfeld, K. Ni(CO)4 Formation on Single Ni Crystals: Reactivity Kinetics and Observation of Surface Facetting Induced by the Reaction. Surf. Sci. 1980, 94, 204–220.
(27) Liang, D. B.; Abend, G.; Block, J. H.; Kruse, N. Formation of Nickel Subcarbynls from Nickel and Carbon Monoxide. Surf. Sci. 1983, 126, 392–396.
(28) Czerek, I.; Loviat, F.; Raimondi, F.; Wambach, J.; Bialloz, S.; Wokaun, A. Characterization of Surface Processes at the Ni-Based Catalyst During the Methanation of Biomass-Derived Synthesis Gas: X-Ray Photoelectron Spectroscopy (XPS). Appl. Catal. A 2007, 329, 68–78.
(29) Matienzo, J.; Yin, L. I.; Grim, S. O.; Swartz, W. E. X-Ray Photoelectron Spectroscopy of Nickel Compounds. Inorg. Chem. 1973, 12, 2762–2769.