



Experiment title:
Alloying in catalysts of bimetallic nano-particles

Experiment number:
HS-43

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BL18/BM29

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15

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Report:

Bimetallic small particles have recently attracted much attention in heterogeneous catalysis. By varying the ratio of the two constituents, the distribution of the compounds at the surface may be altered as well. In this way it may be possible to tune the chemical reactivity at the surface of such an alloy particle. In order to design bimetallic catalysts with specific properties, it is of primary importance to obtain a better understanding of the structure and the segregation-behaviour of small particle systems. Of special interest are combinations of metals for which the bulk binary alloy exhibits a miscibility gap. The purpose of this study is to verify if a surface alloy of two immiscible metals on particles of nanometer size is formed. The Au/Ni system was chosen for this experiment, because STM studies of the deposition of Au on Ni(110) and Au on Ni(111) single crystals have shown that surface alloy formation is restricted to the outermost atomic layer. A series of samples with different atomic ratios of Ni: Au was prepared: ∞ , 14:1, 5:1, 1:1. The samples were prepared by coimpregnation of $\text{Ni}(\text{NO}_3)_2$ and AuCl_3 on a silica support. The total metal weight loading was approximately 3%.

In order to characterize the structure of the small alloy particles, EXAFS experiments were performed at the BL18 beamline at the ESRF, using a Si(311) double crystal monochromator. The X-ray absorption was measured as a function of energy for the Ni K-edge and the Au L_{2,3}-edge. Ionization chambers were used to measure the incoming and transmitted X-ray intensities. The sample was loaded in an in situ EXAFS cell which allowed for heating in different gas flows. Reduction of the samples was carried out at 67.5 K in a flow of pure H_2 .

EXAFS spectra were obtained for the as-prepared samples and after reduction at room temperature. The Ni K-edge spectra of the w-prepared catalysts resemble NiO spectra. The Au L_{2,3} spectra are indicative of the presence of a Au-Cl compound. After reduction, the EXAFS spectra resemble metallic Ni and metallic Au. The EXAFS signals are extracted from the absorption spectra by means of standard background subtraction, normalization, and spline fitting techniques. Fourier transformation and filtering of the first shell contributions were performed and the backtransformed data was fitted with experimentally obtained amplitude and phase functions.

For this preliminary analysis, the data at the Ni ($/\text{Au}$) edge were fitted by means of amplitude and phase functions obtained from Ni ($/\text{Au}$) reference foils. The Ni coordination numbers obtained by the fitting procedure vary between 9 and 11.5, indicating average particle sizes in the range of a 15 100Å. Fitting the backtransformed spectra obtained at the Au edge with reference functions of bulk Au results in poor fits except for the sample with the highest Au load (1:1). The Ni:Au-1:1 sample results in a reasonable fit, because of the relatively large amount of large Au particles (verified by TEM measurements). The poor fits are indicative of a coordination of Au atoms by other than Au atoms and might indicate surface alloy formation.

After reduction, the samples were exposed to a mixture of 2% O_2 in Ar and NEXAFS spectra were collected around the Ni K-edge during oxidation. The Ni K-edge EXAFS spectra before and after oxidation are shown in figures 1 and 2. The white line increases strongly for the pure Ni $/\text{SiO}_2$ sample, while there is only a very small increase for the Ni/Au $/\text{SiO}_2$ samples. This strongly suggests that Au is present on the surface of the Ni particles, preventing the Ni from oxidation. The Au L α -edge spectra hardly change upon oxidation.

After oxidation at room temperature, the samples were heated to 675 K (5 K/minute) in the O_2/Ar Bow. The white line at the Ni K-edges increases slowly for the Ni/Au samples and at 675 K the structure resembles NiO. The transition from metallic to fully oxidized Ni takes place around 450 K. After cooling down to room temperature, the samples were reduced a second time in pure hydrogen in order to see whether the oxidation is reversible. All of the EXAFS spectra look similar after the second reduction except for the sample with the lowest Au load. This might be due to a redistribution of Au. A more thorough analysis and comparison with EXAFS calculations is currently in progress.

Acknowledgments

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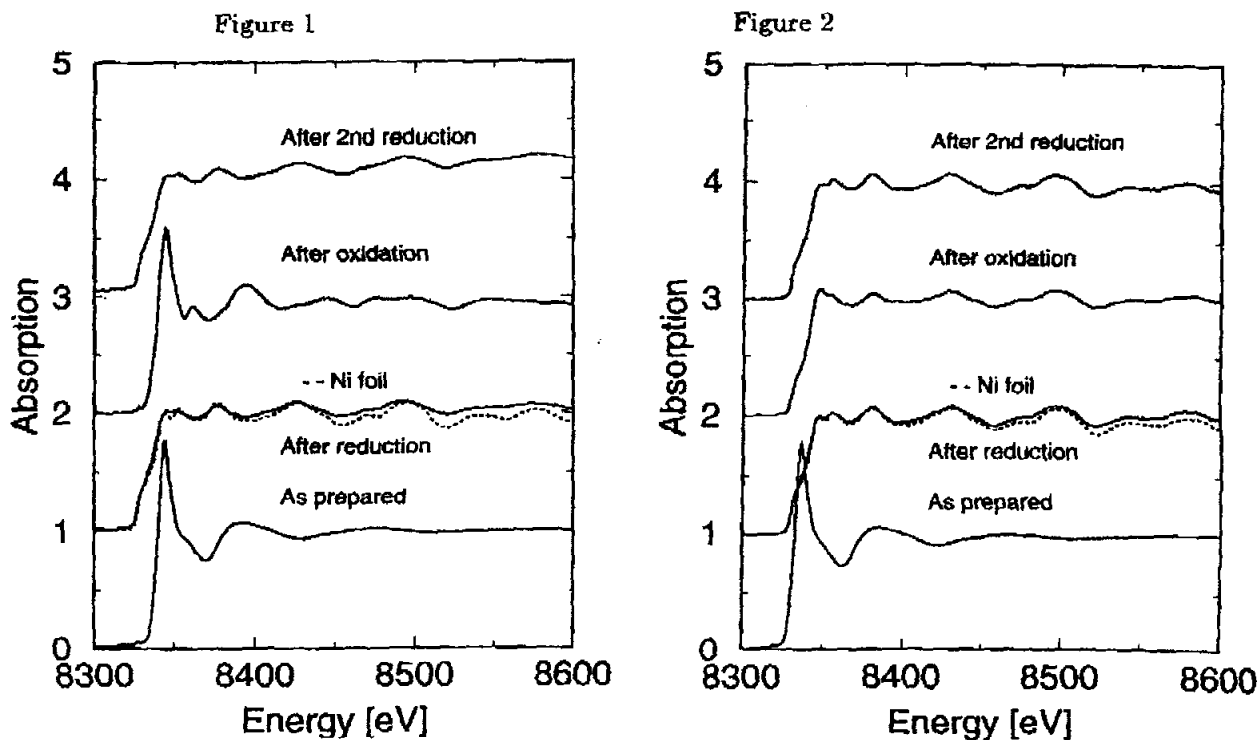


Figure 1 (Left) Normalized EXAFS spectra on the Ni K-edge from Ni $/\text{SiO}_2$.

Figure 2 (Right) Normalized EXAFS spectra on the Ni K-edge from Ni/Au=14 $/\text{SiO}_2$.