

Characterization of Fe-Ni alloy on a Ceria Support as a Noble-Metal-Free Catalyst

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1 Introduction

The fabrication of bimetallic nanoparticles (NPs) has attracted much attention owing to their potential application in catalysis, which originates from the interplay of electronic and lattice effects of the neighboring metals. Because of such synergistic effects, bimetallic catalysts can show significantly higher catalytic activity than their monometallic counterparts.^{1,2}

In the course of our ongoing studies to explore practical catalysts, we found that bimetallic FeNi nanoparticles supported on CeO₂ was proven to be effective for hydrogen production from ammonia borane (NH₃-BH₃, AB) as a noble-metal-free catalyst.³ Here, we report the detail characterization of by in situ XAFS measurements.

2 Experiment

CeO₂ (0.5 g) was mixed with a 100 mL of aqueous solution containing FeSO₄·7H₂O (0.05 g, 0.18 mmol), NiCl₂·6H₂O (0.043 g, 0.18 mmol) and stirred at room temperature for 1 h. The suspension was evaporated under vacuum, and the obtained powder was dried overnight, giving FeNi/CeO₂. Subsequently, the samples were pre-reduced with NaBH₄.

3 Results and Discussion

FeNi/CeO₂ was proven to be effective for hydrogen production AB. In contrast, FeNi/ZrO₂ exhibited inferior activity to FeNi/CeO₂. X-ray absorption measurements were carried out to investigate the local structure and chemical environment of FeNi/CeO₂ in comparison with FeNi/ZrO₂.

Figure 1A shows the Fourier transforms (FT) of Ni K-edge extended X-ray absorption fine structure (EXAFS) spectra of these samples. Both FeNi samples exhibited a main peak at approximately 2.0 Å, which could be assigned to the contiguous Ni–Ni bond in the metallic form. The Ni–Ni distance in FeNi/CeO₂, however, was found to be slightly shorter than those of pure Ni metal and FeNi/ZrO₂, suggesting the presence of Fe–Ni heteroatomic bonding in FeNi/CeO₂. FeNi/CeO₂ also showed another peak at 2.85 Å in the second coordination region, which may be mainly attributed to Ni–O–Ce bonds, because the position of this second peak differs from those of Ni–O–Ni and Ni–O–Fe observed in NiO and NiFe₂O₄, respectively.

The FT-EXAFS spectra at Fe K-edge of FeNi/CeO₂ showed a main peak corresponding to Fe–O at 1.5 Å, accompanied by a slight peak around 3.0 Å (**Figure 1B**). Compared to the Fe–O–Fe bond of FeO, the position of the second peak was shifted slightly to a longer

interatomic distance, which was partially similar to that of the Fe–O–Ni bond observed in NiFe₂O₄. Thus, this peak may be attributed to contiguous Fe–O–Ni as well as Fe–O–Ce bonds via strong interaction with the CeO₂ support. For the structural model of the FeNi/CeO₂, the overall results suggest the formation of partially oxidized amorphous FeNi NPs with a small size, which are stabilized by a strong interaction with CeO₂ via Ni–O–Ce and Fe–O–Ce bonding. In contrast, FeNi/ZrO₂ showed a main peak at around 2.0 Å, which was slightly different from both the Fe–O and the Fe–Fe bonds, indicating the presence of structurally disordered FeO and FeNi phases. Upon consideration of the H₂-TPR results as well as the reduction potentials of ions ($E^0(\text{Ni}^{2+}/\text{Ni}^0) = -0.257$ V, $E^0(\text{Fe}^{2+}/\text{Fe}^0) = -0.44$ V vs. NHE), the structural model of FeNi/ZrO₂ allows the reasonable supposition that most of the Ni atoms are preferentially located in the core region, while the Fe atoms are preferentially located in the shell region. Thus, the Fe atoms are more oxidized than the Ni atoms because of exposure to the surface.

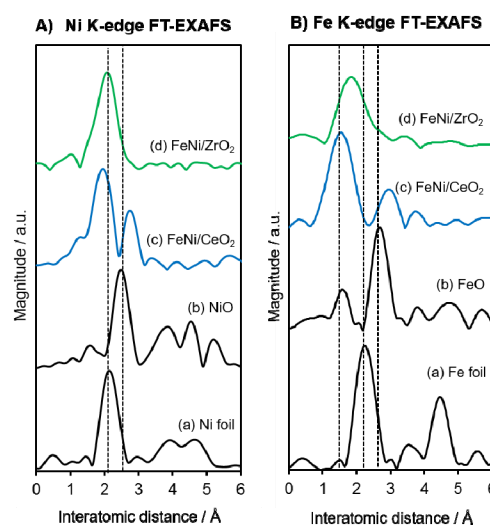


Figure 1 FT-EXAFS spectra (A) at Ni K-edge and (B) Fe K-edge.

References

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