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XAFS analysis of Ni-Zr alloys after thermal and chemical treatment

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Introduction

Amorphous materials have no long-range order at the atomic length scale and show different properties as compared to typical crystalline materials. Among of them, amorphous alloys are in thermodynamically non-equilibrium, crystallized by heating and used as catalysts and catalyst precursors. Investigations on the relationships between their catalytic performances and structural changes during the crystallization process of amorphous alloys are quite interesting research topics. To active catalysts, skeletal metal catalysts were also prepared by acid or base treatment of alloys.

In this study, porous Ni catalysts were prepared from Ni-Zr alloys via heating at various temperatures and following HF treatment for extraction of Zr moieties. XAFS analyses were performed to clarify the effect of heating on the catalytic performances of thus obtained porous Ni catalysts.

Experimental

Ribbon-shaped $Ni_{40}Zr_{60}$ amorphous alloy (amor-NiZr) was prepared by the rapid quenching method using a single steel roll. The heat treatments of amor-NiZr were carried out in a temperature range from 373 to 773 K under vacuum for 2 h. For extraction of Zr moieties, obtained samples were treated by aqueous HF solution (1.0 mol/L) for 5 min, and then thoroughly washed by ion-exchanged water. The catalytic performances of samples were tested by hydrogenation reaction of 1-octene to octane as a model reaction.

XAFS spectra at Ni K-edge were measured in the transmission mode at 298 K. Obtained data were examined using the analysis program (Rigaku REX2000).

Results and Discussion

The structures of untreated and heated samples at each temperature were investigated by XRD measurements. The untreated and heated samples below 573 K only showed a similar broad peak (halo). Overlapped diffraction peaks, (i.e., a broad peak (halo) and peaks assigned to crystalline $NiZr_2$,) as well as sharp peaks due to the formation of crystalline $NiZr_2$ and NiZr were observed after heating at 673 K and 773 K, respectively.

The SEM images and EDX data clearly showed the formation of porous structure and successful extraction of Zr moieties through the HF treatment of untreated and heated samples.

In the hydrogenation reaction of 1-octene to octane, amount of formed octane per surface area of each sample was increased with increasing the heating temperature of amor-NiZr up to 573 K. At higher heating temperatures,

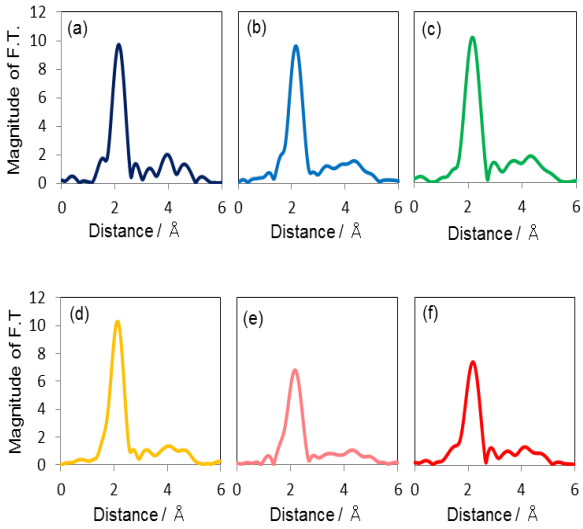

Fig. 1 Fourier transforms of EXAFS spectra of porous Ni catalysts prepared with an HF solution from Ni-Zr alloys (a) as-quenched, (b) heated at 373 K, (c) 473 K, (d) 573 K, (e) 673 K, (f) 773 K.

the decreases in the amount of formed octane was observed due to the crystallization and the aggregation of Ni moieties. Porous Ni catalyst prepared from heated amor-NiZr at 573 K exhibited higher catalytic performances, while the clear structural differences of heated amor-NiZr below 573 K were hardly detected by XRD measurements. XAFS analyses were thus carried out to clarify the structural differences at the atomic length scale.

Figure 1 shows the Fourier transforms of EXAFS spectra of porous Ni catalysts. The intensity of peak attributed to the Ni-Ni bond at around 2 Å (without phase-shift correction) was slightly increased with increasing the heating temperature of amor-NiZr up to 573 K. The intensity of this peak became weak after crystallization at higher temperature. These small changes below 573 K attributed to the short range structural rearrangement in amorphous structure.

This structural rearrangement by heating, i.e., the formation of intermediate crystalline states of amorphous Ni-Zr alloys, lead to the higher catalytic performances of porous Ni catalyst prepared from heated amor-NiZr at 573 K. The state of amorphous Ni-Zr alloys strongly affect to the catalytic performances of porous Ni catalyst.

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