Characterization of Ni/FAU catalysts and catalytic activity for dry reforming reaction of methane

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Abstract: Ni catalysts supported on FAU zeolite were prepared by the ion exchange method by varying the acidity of aqueous solution of the Ni precursor. The generation of isolated atomic Ni(0) species has been demonstrated by *in situ* XAFS measurements during the reduction treatment after the calcination. The isolated Ni(0) species and the Ni(0) particle were coexisted in the Ni/FAU catalysts prepared at the neutralized pH condition, because the latter was generated from the supported hydroxide species. The highest catalytic activity was observed for the Ni/FAU catalyst, in which both Ni(0) species coexisted, suggesting the methane activation by the isolated Ni(0) species.

Keywords: Dry reforming of methane, Ni/FAU catalyst, *In situ* XAFS characterization.

1. Introduction

Zeolite is a good supporting material for many metal catalysts, because the active metal center is highly dispersed during its preparation process by the ion exchange method. The dispersion of the active metal species leads to form small metal particles, and they can contribute to enhance the catalytic activity. For the reforming reaction of hydrocarbons, the supported Ni catalysts attract attention as the alternative candidate of the rare metal catalysts [1], and it has been reported that the activity of Ni catalyst supported on zeolite is higher than the Zn and Co catalysts [2]. This study has revealed the supporting process of the Ni species on FAU zeolite by varying the preparation conditions, and the contribution to the catalytic activity for the dry reforming reaction of methane has been clarified.

2. Experimental

The Ni/FAU catalysts were prepared by the ion exchange method using aqueous solutions of Ni(II) nitrate by keeping the pH value at 3.0, 7.3, and 11.0 during the ion exchange procedure. The filtrated powder was dried at 60 ºC and was subjected to the calcination at 900 ºC in air. The Ni/FAU catalysts were treated under H_2 atmosphere at 900 ºC to reduce the supported Ni species before the catalytic tests. The conversions of CH_4 and CO_2 to H_2 and CO were determined by the gas chromatography measurement under the flow of 1:1:8 mixture of CH_4, CO_2, and Ar with the total flow rate of 50 cm^3/min. The *in situ* XAFS measurements were carried out during the temperature-programed reduction (TPR) process for three Ni/FAU catalysts after the calcination at BL-9C of the Photon Factory (KEK, Tsukuba). The Si(111) double-crystal monochromator was detuned in order to remove the higher order reflection. The H_2 gas (10 vol%) diluted by He was flowed at the total flow rate of 50 cm^3/min, and the temperature was raised to 900 ºC with the rate of 10 ºC/min. The measurement time of a XAFS spectrum was 60 s, and the measurements were repeated with the interval of 60 s.

3. Results and discussion

The XANES spectral change during the TPR process of three Ni/FAU catalysts is shown in Figure 1. At the basic condition (pH 11.0), the Ni(II) hydroxide was first supported on the FAU zeolite, and the Ni(II) hydroxide was converted to NiO after the calcination. The initial XANES spectrum before the TPR process was in agreement with the reference NiO sample. The XANES change clearly demonstrated that the NiO species was reduced to metallic Ni(0) particle. In contrast, the hydrated Ni(II) species was first exchanged on the FAU zeolite at the acidic condition (pH 3.0), and was converted to the isolated Ni(II) species without

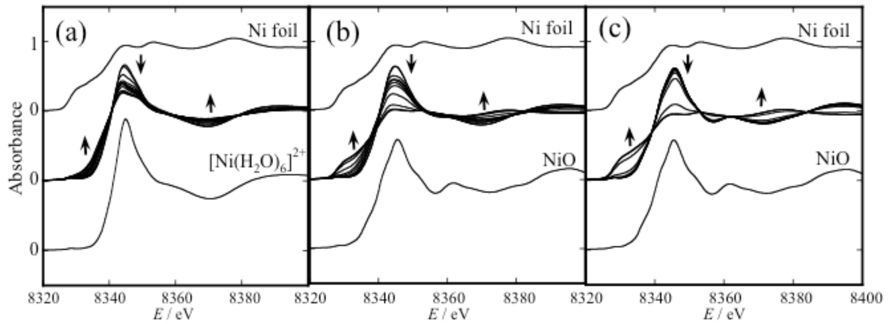

Figure 1. XANES spectral change during the TPR process of Ni/FAU catalyst prepared by the ion exchange method using Ni(II) nitrate solution at pH 3.0 (a), pH 7.3 (b), and pH 11.0

bound water molecules after the calcination. The absorption edge was then shifted to the lower energy during the TPR treatment, and it was thus concluded that the isolated Ni(II) species was reduced to the Ni(0) species, because the threshold energy was almost comparable to those of other Ni(0) species as shown in Figure 2, in which the XANES spectra of the Ni/FAU catalysts after the TPR treatment were compared with the reference Ni(0) sample, which was prepared by the liquid-phase reduction (LPR) of the ion-exchanged Ni(II) species with sodium borohydride. The XANES spectrum of the Ni/FAU catalyst prepared at acidic condition (pH 3.0) was largely different from that of bulk Ni metal and also different from that of Ni/FAU prepared by the LPR procedure. The XANES difference reasonably suggested that the isolated atomic Ni(0) species existed in the present Ni/FAU catalyst (pH 3.0). The *in situ* XAFS analysis also revealed that both the isolated atomic Ni(0) species generated from the ion exchanged Ni(II) species and the Ni(0) particles generated from the NiO particle, which was formed by the supported Ni(II) hydroxide, were coexisted in the Ni/FAU catalyst prepared at the neutralized pH condition (pH 7.3).

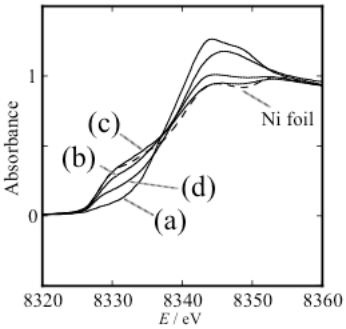

Figure 2. XANES spectra of Ni/FAU catalyst prepared at pH 3.0 (a), pH 7.3 (b), and pH 11.0 (c) after the TPR treatment are compared with that of Ni foil and that of Ni/FAU catalyst prepared by the LPR process (d).

Figure 3 shows the H_2 conversion for the dry reforming reaction of methane over three Ni/FAU catalysts. The higher conversion was observed for the Ni/FAU catalyst prepared at pH 7.3. It has been demonstrated that the isolated atomic Ni(0) species and the Ni(0) particle concertedly work as the active centers for the overall reforming reaction.

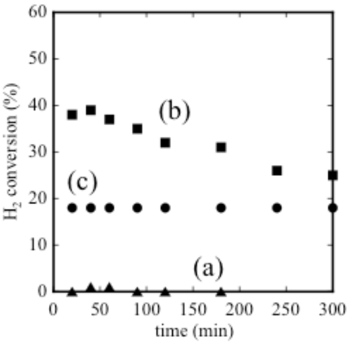

Figure 3. H_2 conversion for dry reforming reaction of methane over Ni/FAU catalyst prepared at pH 3.0 (a), pH 7.3 (b), and pH 11.0 (c).

4. Conclusions

The chemical state of the supported Ni species in Ni/FAU catalysts prepared at pH 7.3 has been evaluated by *in situ* XAFS measurements, and it has been clarified that both the isolated atomic Ni(0) species generated from the ion exchanged Ni(II) species and the Ni(0) particles generated from NiO, which is formed by the supported Ni(II) hydroxide, are coexisted. The highest catalytic activity has been observed for such Ni/FAU catalyst, suggesting that the methane molecule is activated by the isolated Ni(0) species and such methane molecule is effectively converted on the Ni(0) particle.

References

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