Active Phase Structure of the SiO₂-supported Nickel Phosphide Catalysts for Non-oxidative Coupling of Methane (NOCM) Reactions

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SiO₂-supported NiP binary catalysts show high activity for the non-oxidative coupling of methane (NOCM) reactions, one of the most difficult but important catalytic reactions. We have studied the SiO₂-supported NiP binary catalysts by extended X-ray absorption fine structure (EXAFS) with different Ni : P ratios. NiP binary catalyst with the composition of Ni : P = 1 : 1 was the most active among the three different compositions. EXAFS showed that the NiP catalyst with Ni : P = 1 : 1 had a Ni₂P structure. The structure was stable after the high temperature (1173 K) NOCM reaction conditions for 12 h. It is interesting that Ni₂P shows high catalytic activities in many other reactions such as hydrodesulfurization, hydrogen evolution reaction, and so on. It may be due to the appropriate electronic and geometrical modification of a Ni active site by P.

Keywords EXAFS; Nickel phosphide; Ni₂P; Non-oxidative coupling of methane

I. INTRODUCTION

Extended X-ray absorption fine structure (EXAFS) spectroscopy is the most promising technique used for the atomic-level characterization of the inorganic-oxide-supported catalysts. Recently, due to the oil depletion of petroleum, many attentions have been paid to the utilization of CH₄ for organic material feedstock syntheses. One way to convert methane to the higher hydrocarbons is non-oxidative coupling of methane (NOCM) reactions using catalysts at high temperature.

Recently, Yamanaka et al. screened catalytic activities of various Ni-M/SiO₂ compounds (M = metals or metalloids) for the NOCM reactions using a fixed bed-gas-flow system at 1173 K and found that SiO₂-supported NiP catalysts showed highest activity for the NOCM reaction to produce hydrocarbons at 1173 K among the others [1]. There was a strong dependence on the ratio of Ni : P, and Ni : P = 1 : 1 showed the best performance as shown in Figure S1 in Supplementary Material. Figure S2 (Supplementary Material) shows the X-ray diffraction (XRD) result. Ni : P = 1 : 1 gave the peaks corresponding to Ni₃P crystalline. The crystalline size was 30–40 nm from the peak width. However, XRD was not so sensitive to the structures of nanoparticles or amorphous phases.

In this research, we applied EXAFS to elucidate the active structure of NiP catalysts with different Ni : P ratios before and after NOCM reactions.

II. EXPERIMENTAL

The SiO₂-supported NiP catalysts with initial NiP ratios of
1 : 1, 2 : 1, and 3 : 1 were prepared by a conventional impregnation method, followed by temperature programmed reduction. The preparation details can be found in the Supporting Information of Ref. 1. The sample was denoted as Ni-P/SiO2 (NiP = X : Y, Zh) where X : Y represents the Ni : P ratio and Z is the reaction time. Before performing each NOCM reaction, the catalyst was purged by 10 mL min\(^{-1}\) of Ar while the temperature increased from room temperature to 1173 K at a rate of 25 K min\(^{-1}\). Pure methane was flowed at 10 mL min\(^{-1}\) into the reactor at 1173 K.

EXAFS measurements were carried out at BL9C of the Photon Factory (PF) in Institute for Structure Materials Science, High Energy Accelerator Research Organization (KEK) operated at 2.5 GeV, 450 mA. The emitted X-ray was monochromatized by a Si (111) double crystal and focused with a Rh coated bent cylindrical mirror. The EXAFS analyses were carried out by the REX2000 (Rigaku Co.) [2]. The theoretical amplitude and phase shift functions of Ni–Ni and Ni–P atom-pairs were calculated by FEFF8 [3]. The two- shell fitting for Ni–Ni and Ni–P bonds provided the bond distances, coordination numbers, and the other structure parameters. The number of fitting parameters was less than the values determined by the formula, \(N_{\text{ind}} = 2\Delta k\Delta R/\pi + 2\) [4], where \(N_{\text{ind}}\) is a number of independent parameters, \(\Delta k\) is a range of used data in the wave number \(k\), and \(\Delta R\) is a range of used data in the interatomic distance \(R\).

### III. RESULTS AND DISCUSSION

Figure 1 shows the EXAFS oscillations [an EXAFS oscillation, \(\chi(k)\), vs. the photoelectron wave number, \(k\)] of the fresh and spent samples with different initial Ni : P ratios after background subtraction. The three different Ni : P ratio samples give different oscillations. Figure 1(b) shows the EXAFS oscillation of the sample Ni-P/SiO2 (Ni : P = 1 : 1, 0 h), which was similar to that of the Ni2P reference as shown in Figure 1(a), indicating that Ni-P/SiO2 (Ni : P = 1 : 1, 0 h) had mostly the Ni2P structure. Ni-P/SiO2 (Ni : P = 2 : 1, 0 h) and Ni-P/SiO2 (Ni : P = 3 : 1, 0 h) had quite different oscillations from those of Ni2P reference as shown in Figure 1(c, d). We could not find little change in the spent samples with various Ni : P ratios even after the high temperature reactions at 1173 K. The NiP catalysts had high stability.

Figure 2 shows the Fourier transforms of the Ni K-edge EXAFS spectra for the fresh and spent samples. The Ni-P/SiO2 (Ni : P = 1 : 1, 0 h) showed two distinct peaks in this Fourier transform as shown in Figure 2(b). The first and main peak were corresponding to the Ni–P and Ni–Ni...
Figure 2(c). Curve fitting analyses indicated the Ni–Ni bond distance was 2.52 Å while that of Ni–P was 2.19 Å as shown in Table 1.

Table 1: Curve fitting results of the Ni K-edge EXAFS spectra for the NiP reference and different samples with initial Ni : P ratios of 1 : 1, 2 : 1, and 3 : 1.

| Samples            | Ni–Ni CN | R (Å)  | \(\sigma^2 (Å^2)\) | \(\Delta E (eV)\) | Ni–P CN | R (Å)  | \(\sigma^2 (Å^2)\) | \(\Delta E (eV)\) |
|--------------------|----------|--------|----------------------|-------------------|----------|--------|----------------------|-------------------|
| Fresh Samples      |          |        |                      |                   |          |        |                      |                   |
| Ni2P reference     | 4.0 ± 0.3| 2.62 ± 0.02| 0.92 x 10^{-4} | 5.4               | 1.0 ± 0.3| 2.21 ± 0.02| 0.71 x 10^{-4} | −5.1 ± 0.5        |
| Ni-P (1:1, 0 h)    | 4.6 ± 0.6| 2.62 ± 0.02| 0.85 x 10^{-4} | 3.4               | 1.3 ± 0.3| 2.19 ± 0.02| 0.81 x 10^{-4} | −7.5 ± 0.3        |
| Ni-P (2:1, 0 h)    | 4.2 ± 0.3| 2.52 ± 0.02| 0.93 x 10^{-4} | −1.1              | 0.6 ± 0.3| 2.18 ± 0.03| 0.36 x 10^{-4} | −7.3 ± 0.1        |
| Ni-P (3:1, 0 h)    | 4.6 ± 0.9| 2.45 ± 0.02| 1.16 x 10^{-4} | −7.2              | 2.0 ± 0.5| 2.28 ± 0.02| 1.39 x 10^{-4} | −3.6 ± 0.5        |
| Spent Samples      |          |        |                      |                   |          |        |                      |                   |
| Ni-P (1:1, 3 h)    | 4.5 ± 0.8| 2.62 ± 0.03| 0.82 x 10^{-4} | 3.5               | 1.5 ± 0.5| 2.18 ± 0.03| 0.84 x 10^{-4} | −9.8 ± 0.5        |
| Ni-P (2:1, 3 h)    | 4.3 ± 0.3| 2.53 ± 0.03| 0.95 x 10^{-4} | −0.7              | 0.7 ± 0.3| 2.17 ± 0.03| 0.58 x 10^{-4} | −8.8 ± 0.3        |
| Ni-P (3:1, 3 h)    | 4.6 ± 1.0| 2.46 ± 0.02| 1.17 x 10^{-4} | −6.6              | 2.1 ± 0.6| 2.28 ± 0.03| 1.31 x 10^{-4} | −2.3 ± 0.4        |

*Coordination number.

Interatomic distance.

σ; Debye-Waller factor.

Edge shift.

Residual factor.

We could characterize the most active Ni-P/SiO2 (Ni : P = 1 : 1) catalyst as Ni2P successfully, which was consistent with X-ray diffraction analysis as shown in Figure S2 (Supplementary Material). It is difficult to derive the structures about the NiP (2 : 1, 0 h) and NiP (3 : 1, 0 h) only from EXAFS because of less informative features of EXAFS oscillations. But we could say that there is no indication of the formation of Ni metal nanoclusters, because we always found the Ni–Ni distance for NiP (2 : 1, 0 h) or NiP (3 : 1, 0 h) was longer or shorter than that of Ni metal as shown in Table 1, respectively. We are now carrying out the XANES (X-ray absorption near edge structure) analysis using these possible crystalline structures.

Recently Ni2P catalysts draw many attentions. It shows a high catalytic activity in hydrogen related reactions, such as hydrodesulfurization reactions [5, 6], hydrodeoxygenation [7, 8], and hydrogen evolution reactions [9, 10], Ni2P has a crystal structure as shown in Figure 3 [11]. Along the c axis, two-layer structures are alternatively stacked. One is called Ni3P and the other is Ni3P2. Scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) of the Ni2P single crystal showed Ni3P2 was mainly present on the Ni2P(0001) surface [12–16].

Both Ni2P and Ni3P2 structures have three-fold Ni hollow sites surrounded by P. The three-fold Ni hollow sites might be the active site and P should modify the electronic structure of Ni as well as the isolation of too much active Ni hollow sites [12]. This might prohibit undesired coke formations and more selectively cleave the C–H bond. Moreover, the isolation of Ni sites might slow down the chain expansion reaction and C2H4 formation becomes preferable.

We used more P than stoichiometry to have a Ni2P structure. In the previous studies, the NiP ratio of 1 : 1 was required to prepare the Ni2P structure [17], because we
found that the evaporation of P at high temperature under reductive or ultrahigh vacuum conditions [18]. Less P induces the phase transition to Ni$_{12}$P$_5$, or the other phase. The extra PO$_4$ species present on the surface might play the role of the P supplier. Thus, Ni : P = 1 : 1 gives the Ni$_2$P structure stably.

Above discussion is based on the assumption that the surface structure is the same as the bulk terminated and the structure under the working conditions is identical to that before and after the reaction. In order to reveal the real active site structure, we are going to carry out in situ EXAFS measurements of Ni$_2$P catalysts at 1173 K under the flow of methane like the EXAFS analysis of In/SiO$_2$ NOCM catalyst [19].

IV. CONCLUSIONS

We investigated the structure of active NiP binary catalysts by EXAFS. The most active catalyst had Ni$_2$P structure and its structure was stable during non-oxidative coupling of methane (NOCM) reactions at 1173 K. P might control the Ni activity not to form the C−C bond by geometrically or electronically.

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Appendix

Details of catalysts preparation, dependence of yield of hydrocarbons on the Ni : P ratios, and catalyst characterizations other than EXAFS are available in Supplementary Material at https://doi.org/10.1380/ejssnt.2020.24.

Note

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