Formation of Rh2P Supported on Na-form Zeolites and Catalytic Activity for Hydrodesulfurization

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The effects of zeolite structure on rhodium phosphide (Rh2P) formation, dispersion and hydrodesulfurization (HDS) activity were investigated. TPR showed that the order of maximum peak temperature for phosphates reduction was Na-beta > NaMFI > NaMOR. The XRD patterns of reduced catalysts revealed that the order of Rh2P formation temperature agreed with that of phosphate reducibility. CO uptake of NaMOR-supported catalyst was much lower than those of other zeolite-supported catalysts. These results suggested that since the NaMOR support had a one-dimensional channel, the phosphates and Rh species did not easily diffuse into the micropores. The order of thiophene HDS conversion was NaMFI > Na-beta > NaMOR. The order of average particle size of Rh2P calculated from TEM images was NaMOR > Na-beta = NaMFI. Since formation of Rh2P on the Na-beta needed high reduction temperature, the beta structure might be partially collapsed. Well-dispersed Rh2P was formed on NaMFI at lower reduction temperature, so that this catalyst exhibited the highest HDS activity among the zeolite-supported catalysts.

Keywords
Rhodium phosphide catalyst, Zeolite support, Hydrodesulfurization, Phosphate reducibility, Micropore structure

1. Introduction

Strict regulation of sulfur content in fuels to decrease air pollution will restrict the emissions of sulfur oxides in exhaust gas from ships within a few years. Therefore, reduction of the sulfur content in heavy oil, which used as the fuel for ships, will be essential. Future production of low sulfur fuels will depend on the development of highly active hydrodesulfurization (HDS) catalysts.

Transition metal phosphides have been reported as highly active new HDS catalysts. Metal-rich phosphides are generally used to develop HDS catalysts because phosphorus-rich phosphides are less stable. In particular, nickel phosphide (Ni2P) catalyst, which has high HDS activity, has been widely studied. We previously reported noble metal phosphides supported on SiO2 as a new type of HDS catalyst. The rhodium phosphide (Rh2P) catalyst showed the highest activity among various noble metal phosphides, with equivalent activity to the commercial Co-Mo catalyst. Moreover, the Rh2P catalyst showed dramatically high HDS activity compared with the Ni2P/SiO2 catalyst.

The catalyst supports, such as SiO2 and Al2O3, affect the formation temperature and dispersion of Rh2P, so are the dominant factor in the catalytic activity. Al2O3 is well known to have strong affinity for phosphates. The formation temperature of Rh2P on the Na-beta needed high reduction temperature, the beta structure might be partially collapsed. Well-dispersed Rh2P was formed on NaMFI at lower reduction temperature, so that this catalyst exhibited the highest HDS activity among the zeolite-supported catalysts.

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changed by the micropore structure of zeolites. We previously found that large phosphate particles are easy to reduce\(^{33}\). Therefore, formation temperature and dispersion of Rh\(_2\)P affect the catalytic activity. The present study investigated Rh\(_2\)P formation on various Na-form zeolites to clarify the effect of micropore structure. The HDS activities of the Na-form zeolite-supported Rh\(_2\)P catalysts were examined.

2. Experimental

2.1. Catalyst Supports

Na-form zeolites were used as supports as follows: MFI (ZSM-5, Tosoh), MOR (mordenite, Tosoh) and BEA (beta, N.E. CHEMCAT). Na-beta (hereinafter, NaBEA) was obtained by ion exchange of HBEA using sodium nitrate (NaNO\(_3\)) aqueous solution (0.08 mol/L). The suspension was evaporated, followed by filtration and washed with 0.05 mol/L NaNO\(_3\) aqueous solution. The washed BEA was dried at 110 °C for 24 h in air, followed by calcination at 400 °C for 1 h. This ion exchange process for preparation of NaBEA was performed two times to increase Na content.

2.2. Catalyst Preparation

Rh-P/zeolite catalysts were prepared by an impregnation method using rhodium (III) chloride trihydrate (RhCl\(_3\)·3H\(_2\)O) and ammonium dihydrogen phosphate (NH\(_4\)H\(_2\)PO\(_4\)) aqueous solution as described elsewhere\(^{7,9,12-14}\). The Rh and P loadings were 5 wt% and 1.5 wt%, respectively. The impregnated catalyst was dried at 110 °C for 24 h, followed by heat treatment at 450 °C for 1 h in a nitrogen (N\(_2\)) stream to decompose the salts. The decomposed catalyst was pressed into disks and crushed to obtain 30-42 mesh size granules. The sieved catalyst was calcined at 500 °C for 4 h in air. The ramp rate of heat treatment and calcination were 10 °C/min.

2.3. Characterization

The zeolite supports were characterized by X-ray fluorescence (XRF) analysis, N\(_2\) adsorption and cumene cracking reaction. Wavelength-dispersive XRF measurement was performed using Supermini (Rigaku) to obtain the silicon (Si) and aluminum (Al) contents in zeolite supports. The actual Si and Al contents were calculated by the absolute calibration curve method. N\(_2\) adsorption was carried out using a Micromeritics ASAP 2010 at ~196 °C to measure the surface area of the zeolite. The zeolite support was evacuated at 300 °C for 5 h before the measurement. The specific surface area (\(S_{BET}\)) and external surface area (\(S_{EXT}\)) were calculated by the BET and t-plot methods, respectively. The cumene cracking reaction was carried out using a fixed bed flow reactor at 220 °C under 0.1 MPa. The zeolite sample (0.05 g) was charged into the reactor and was heated in a helium (He) stream (30 mL/min) from room temperature to 500 °C at 10 °C/min, then treating at 500 °C for 1 h. After cooling to 220 °C, the treated sample was contacted with a 0.42 vol% cumene-helium gas mixture obtained by passing a He stream through a cumene saturator maintained at 20 °C. Reaction condition (\(W/F\)) was 146.8 g·h/mol. Cumene conversion was calculated by gas chromatography using a flame ionization detector (FID) and Silicone DC-550 column (2.5 m, 135 °C).

The Rh-P/zeolite catalysts were characterized by temperature-programmed reduction (TPR), X-ray diffraction (XRD), CO adsorption and transmission electron microscopy (TEM). The TPR profile was recorded using a thermal conductivity detector (TCD) to monitor consumption of hydrogen (H\(_2\)). The calcined Rh-P/zeolite catalyst (0.1 g) was heated in a 30 mL/min He stream from room temperature to 500 °C at 10 °C/min, then at 500 °C for 1 h. After cooling to 30 °C, the He stream was switched to 5 vol% hydrogen-nitrogen (H\(_2\)-N\(_2\)) gas mixture for 30 min before measurement. Water was removed with a molecular sieve trap. The TPR profile was measured from 30 to 850 °C at 10 °C/min in a 5 vol% H\(_2\)-N\(_2\) stream. CuO was used as a reference to calculate H\(_2\) consumption in TPR profiles of Rh-P/zeolite catalysts. The XRD patterns of calcined and reduced catalysts were obtained by MiniFlex (Rigaku) with Cu K\(_\alpha\) radiation at 30 kV and 15 mA. Crystalite sizes of Rh species were calculated by Scherrer’s equation. The amount of CO adsorption on the Rh-P/zeolite catalysts was measured by a pulse method. The calcined Rh-P/zeolite catalyst (0.1 g) was treated in a He stream at 500 °C for 1 h, followed by reduction in a H\(_2\) stream at 350-850 °C for 1 h. The treated catalyst was cooled to 25 °C in a He stream, followed by measurement of CO adsorption using gas chromatograph equipped with TCD. TEM images were observed using a JEOL JEM-2100F. The average particle size of Rh\(_2\)P was determined from measurement of more than 1000 particles in the TEM images of reduced Rh-P/zeolite catalysts.

2.4. HDS Activity Measurement

Catalytic activity for thiophene HDS was measured in a conventional fixed bed flow reactor at 350 °C under 0.1 MPa. The calcined Rh-P/zeolite catalyst (0.1 g) was charged into the reactor and heated in a He stream (30 mL/min) from room temperature to 500 °C at 10 °C/min, then at 500 °C for 1 h. After He treatment, the catalyst was reduced with H\(_2\) (30 mL/min) at 350-850 °C for 1 h. After cooling to 350 °C, the reduced catalyst was contacted with hydrogen-thiophene gas mixture (H\(_2\)/C\(_8\)H\(_8\)S = 30) obtained by passing a H\(_2\) stream through a thiophene saturator maintained at 0 °C. Reaction condition (\(W/F\)) was 37.9 g·h/mol. \(W/F\) was varied by changing different catalyst weights to compare the HDS products at the same conversion (10%). Thiophene conversion was calculated by gas chromatography using a FID and Silicone DC-550...
(2.5 m, 135 °C) or Bentone 34 + DDT (3.0 m, 135 °C) columns. Composition of products was analyzed by gas chromatography using a FID and Al₂O₃/KCl PLOT (0.53 mm × 25 m, 60-190 °C) column.

3. Results and Discussion

3.1. Characterization of Supports

Al content and Si/Al ratio in the zeolite supports were measured by XRF as shown in Table 1. The NaMFI was the same sample as used in our previous study[12]. The order of Al content was as follows: NaMOR > NaMFI > NaBEA. Table 1 also shows the $S_{BET}$ and $S_{EXT}$ of Na-form zeolites calculated from N₂ adsorption isotherms. NaBEA had the largest $S_{BET}$ among the zeolites. The order of $S_{EXT}$ was NaBEA > NaMFI > NaMOR, indicating that the crystal size of NaBEA was remarkably smaller than those of the other zeolites.

The acidity of zeolites was evaluated by catalytic activity for cumene cracking in order to confirm ion exchange rate. Figure 1 shows the cumene cracking conversion over (a) Na-form and (b) H-form zeolites. NaMOR (a) showed no cumene conversion (<1 %) compared with HMOR (b). NaMFI and NaBEA showed slight conversion (1.8 % and 2.4 %, respectively) at initial reaction (10 min). On the other hand, H-form zeolites (b) showed more than 70 % of conversion. Therefore, protons in these zeolites were sufficiently exchanged with sodium ions. The cumene conversion of NaMFI decreased with time on stream, whereas that of NaBEA was stable. Hexane cracking activity of zeolite with small crystal size is reported to be stable due to low coke deposition[15,16]. Therefore, the stable cumene conversion of NaBEA is a result of the small crystal size.

3.2. Rh Species after Calcination

Figure 2 (a) shows the XRD patterns of calcined Rh-P catalysts supported on (i) NaMOR, (ii) NaMFI and (iii) NaBEA. For the Rh-P/NaMOR catalyst, only metallic Rh peaks were observed. For the Rh-P/NaMFI catalyst, a broad Rh₂O₃ and sharp metallic Rh peaks were observed. For the Rh-P/NaBEA catalyst, only a broad Rh₂O₃ peak was observed. The crystallite sizes of the Rh species were calculated from Scherrer’s equation. In the Rh-P/NaBEA catalyst, the crystallite size of Rh₂O₃ was 3.3 nm. In the Rh-P/NaMOR catalyst, the crystallite size of metallic Rh was remarkably larger at 20.5 nm than that of Rh₂O₃ in the Rh-P/NaBEA catalyst.

In the Rh-P/NaMFI catalyst, the crystallite sizes of metallic Rh and Rh₂O₃ were 27.7 nm and 3.3 nm, respectively.

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3.3. Effect of Zeolite Structure on Phosphate Reduction

Previously, we reported that the reducibility of phosphate strongly affects phosphide formation\(^3\)\(^5\)\(^6\)\(^2\)\(^1\)\(^2\)\(^3\)\(^4\).

Figure 3 shows the TPR profiles of Rh-P/zeolite catalysts. The peaks below 180 °C were divided into two parts; below 100 °C and 100-180 °C. The former was assigned to reduction of bulk rhodium-oxides (Rh\(_2\)O\(_3\)) and the latter was assigned to the RhO\(_x\), interacting with support\(^1\)\(^7\). The Rh-P/NaMFI and Rh-P/NaBEA catalysts showed large RhO\(_x\) reduction peaks at 81 °C and 97 °C, respectively. The Rh-P/NaMOR catalyst was significantly smaller than that in the other catalysts. The XRD pattern of calcined Rh-P/NaMOR catalyst was 20.5 nm. On the basis of these results, the large metallic Rh particles were not completely oxidized and the particle surface was oxidized. The Rh-P/NaMFI catalyst also contained enlarged crystallites of metallic Rh (3. 2.). However, in the TPR profile, the RhO\(_x\) reduction peaks of Rh-P/NaMFI catalyst were much larger than those of Rh-P/NaMOR catalyst and were similar to those of Rh-P/NaBEA catalyst. This point will be discussed further in section 3. 4.

In the TPR profile of Rh-P/NaMFI catalyst, the H\(_2\) consumption peaks above 180 °C were assigned to phosphate reduction\(^1\)\(^2\). These peaks could be divided into two parts; 180-500 °C (in the case of Rh-P/NaMOR catalyst, 200-500 °C) and above 500 °C. The former was attributed to the reduction of phosphates interacting with Rh species\(^1\)\(^4\). The latter was attributed to the reduction of phosphates weakly interacting with
On the basis of these results, the maximum peak temperature of phosphate reduction for the Rh_P/NaMOR catalysts was NaBEA (814 °C) > NaMFI (595 °C) > NaMOR (446 °C). H₂ consumption by phosphate reduction in the TPR profiles of these catalysts is listed in Table 2. Phosphates in the Rh-P/NaMOR catalyst were mostly reduced below 500 °C. The phosphates diffused and adsorbed into the micropores of zeolite during impregnation of catalyst precursors. Considering that the NaMOR support has a one-dimensional channel, the phosphates adsorbed in the micropore would strongly block the diffusion of other phosphates. Moreover, the NaMOR support had significantly low external surface area (Table 1), that is to say, the crystal size was large, which also contributed to reduced diffusion of phosphates into the micropores of zeolite. Therefore, the phosphates easily formed enlarged particles on the external surface. Reduction of large phosphate particles was facilitated because of the weak interaction between the phosphates and the support. On the basis of these results, the maximum peak of phosphate reduction in the Rh_P/NaMOR catalyst was observed at the lowest temperature among the Rh_P/zeolite catalysts. For the NaMFI- and NaBEA-supported catalysts, H₂ consumption was mostly observed above 500 °C (Table 2). The NaMFI and NaBEA supports have three-dimensional micropore structures. Phosphorus is widely reported to interact with the acid sites on phosphorus-modified zeolite. Therefore, the phosphates would easily diffuse into the three-dimensional micropores and adsorb on the nearby cation exchange sites. Generally, small crystal-sized zeolite has low diffusion resistance. The crystal size of the NaBEA support is significantly smaller than that of the NaMFI support, as discussed above (3.1). Therefore, phosphates might easily adsorb on the nearby cation exchange sites in the NaBEA support. Consequently, the Rh-P/NaBEA catalyst showed the highest peak temperature of phosphate reduction among the Rh-P/zeolite catalysts.

### 3.4. Rh₂P Formation and CO Uptake

The micropore structure and crystal size of zeolite support were important in the reducibility of phosphates. Figure 2 shows the XRD patterns of Rh-P/zeolite catalysts reduced at various temperatures. These patterns were obtained by subtraction of the zeolite pattern from the original pattern to clarify the peaks of Rh species. The Rh₂O₃ peak in the XRD patterns of the NaMFI- and NaBEA-supported catalysts disappeared after reduction (ii) and (iii)). For all catalysts, the peaks of Rh species changed from metallic Rh to Rh₂P with increasing reduction temperature because of phosphate reduction. The relationships between reduction temperature and intensity of Rh species are shown in Fig. 4. For the Rh-P/NaMOR catalyst (i), the intensity of Rh₂P was higher than that of metallic Rh at any reduction temperature. For the Rh-P/NaMFI catalyst (ii), the intensity of metallic Rh was only observed at 450 °C. The intensity of Rh₂P increased above 550 °C. Finally, the intensity of metallic Rh was hardly observed at 650 °C. Similarly, for Rh-P/NaBEA catalyst (iii), intensity of Rh₂P increased above 650 °C and that of metallic Rh was hardly observed above 750 °C. Therefore, the order of Rh₂P formation temperature was NaBEA > NaMFI > NaMOR. This order agreed with that of the maximum peak temperature of phosphate reduction in the TPR profiles of the Rh-P/zeolite catalysts, as shown in Fig. 3.

The crystallite sizes of Rh₂P in the Rh-P/zeolite catalysts calculated from Scherrer’s equation are listed in Table 3. For all catalysts, the crystallite size of Rh₂P enlarged with increasing reduction temperature. The crystallite size of Rh₂P in the Rh-P/NaMOR catalyst reduced at 450 °C was larger than that in the Rh-P/NaBEA catalyst reduced at 850 °C. CO is adsorbed on exposed Rh site in Rh₂P catalysts. Effect of reduction temperature on CO uptake of the Rh-P/zeolite...
catalysts is shown in Fig. 5. For all catalysts, CO uptake decreased with increasing reduction temperature. This trend agreed with that of Rh₂P crystallite size (Table 3). The Rh-P/NaMOR catalyst exhibited much lower CO uptake than the other Rh-P/zeolite catalysts. The phosphates did not easily diffuse into the micropores of the NaMOR support because of the one-dimensional channel, as described above (3.3.). Therefore, diffusion of rhodium salts into micropores would also be blocked by phosphates. Consequently, the Rh species would be enlarged on the external surface in the Rh-P/NaMOR catalyst. The TPR profile of Rh-P/NaMFI catalyst showed a large reduction peak of RhO₂ similar as that of Rh-P/NaBEA catalyst (Fig. 3). This result indicates that well-dispersed RhO₂ was formed on the NaMFI support.

![Fig. 4](image-url)

**Fig. 4** Effect of Reduction Temperature on Intensity of Rh Species (Rh: 41.0°, Rh₂P: 46.7°) Observed in XRD Patterns of Rh-P Catalysts Supported on (i) NaMOR, (ii) NaMFI and (iii) NaBEA

**Table 3** Crystallite Size of Rh₂P in Reduced Rh-P/zeolite Catalysts Calculated from XRD Patterns Using Scherrer’s Equation

| Support | Reduction temperature 350 °C | 450 °C | 550 °C | 650 °C | 750 °C | 850 °C |
|---------|-------------------------------|--------|--------|--------|--------|--------|
| NaMOR   | 16.4                          | 27.0   | 35.4   | 38.3   | -a)    | -a)    |
| NaMFI   | -a)                          | 27.0   | 35.4   | 38.3   | -a)    | -a)    |
| NaBEA   | -a)                          | 8.5    | 12.1   | 13.5   | -b)    | -b)    |

a) Not measured.  
b) No peaks of Rh₂P observed.
3. 5. Thiophene HDS Conversion

The formation and crystallite size of Rh2P were affected by the reduction temperature (Figs. 2, 4 and Table 3). Thus, the relationship between reduction temperature and HDS activities of Rh-P/zeolite catalysts was examined (Fig. 6). For the Rh-P/NaBEA catalyst, higher Rh2P intensity and lower metallic Rh intensity were observed with increasing reduction temperature (Fig. 4). The HDS activity was enhanced with increasing reduction temperature. Therefore, Rh2P formation contributed to the enhancement of HDS activity. Simultaneously, CO uptake decreased with increasing reduction temperature (Fig. 5). After reduction at 850 °C, HDS activity was decreased due to aggregation of Rh2P particles. The maximum HDS activity of the Rh–P/NaBEA catalyst was observed at 800 °C. In the Rh–P/NaMFI catalyst, the maximum HDS activity was similarly obtained after reduction at 600 °C. However, for the Rh–P/NaMOR catalyst, the HDS activity was little improved with increasing reduction temperature. The intensity of metallic Rh was lower than that of Rh2P after reduction at 350 °C (Fig. 4). On the basis of these results, the metallic Rh particle was covered with Rh2P. The order of optimal reduction temperature for the maximum HDS activity was NaBEA (800 °C) > NaMFI (600 °C) > NaMOR (450–550 °C). This order agrees with those of phosphate reduction in TPR profiles (3, 3) and Rh2P formation temperature (3, 4). The order of maximum HDS conversion was NaMFI > NaBEA > NaMOR. Average particle size of Rh2P in Rh-P/zeolite catalysts reduced at optimal temperature was examined by TEM observation (Table 4). The order of average particle size was NaMOR > NaBEA > NaMFI. Since Rh2P particles were aggregated, the Rh–P/NaMOR catalyst exhibited remarkably low HDS activity. The NaBEA- and NaMFI-supported catalysts had similar particle size. However, the Rh–P/NaBEA catalyst exhibited lower activity than the Rh–P/NaMFI catalyst. Thus, the effect of reduction on the zeolite crystallinity in these catalysts was investigated. The peak intensity of NaBEA (22.5°) and NaMFI (23.0°) was used. The zeolite crystallinity in calcined catalyst was assumed as 1. For the Rh–P/NaMFI catalyst, the zeolite crystallinity after reduction at 600 °C was 0.97. Therefore, the MFI structure was hardly affected by reduction treatment. However, for the Rh–P/NaBEA catalyst reduced at 800 °C, the zeolite crystallinity was 0.87. Therefore, the BEA structure was partially collapsed at high reduction temperature. In addition, part of Rh2P particles might be involved in the collapsed zeolite structure. In fact, after reduction at the optimal temperature, the CO uptake of Rh–P/NaBEA catalyst was much lower than that of Rh–P/NaMFI catalyst. On the basis of these results, since small particle size Rh2P was formed at relatively low reduction temperature, the Rh–P/NaMFI catalyst showed the highest HDS activity among the Rh–P/zeolite catalysts.

Selectivity for HDS products over Rh-P/zeolite cata-

Table 4  Average Particle Size of Reduced Rh-P/zeolite Catalysts Measured from TEM Images

| Support | Reduction temperature [°C] | Average particle size [nm] |
|---------|---------------------------|--------------------------|
| NaMOR   | 500                       | 12.2                     |
| NaMFI   | 600                       | 8.6                      |
| NaBEA   | 800                       | 8.0                      |
products without THT formation.

4. Conclusions

The Rh-P/zeolite catalysts were studied to clarify the effects of zeolite structure on Rh2P formation, dispersion and HDS activity. TPR and XRD analysis revealed that the order of Rh2P formation temperature was NaBEA ≈ NaMFI > NaMOR. The order of thiophene HDS conversion was NaMFI > NaBEA > NaMOR. Moreover, TEM observation showed that the average particle size of Rh2P was in the order NaMOR > NaBEA > NaMFI. The Rh-P/NaMOR catalyst has a one-dimensional channel and large crystal size, leading to low diffusion of the phosphates and Rh species. Therefore, aggregated Rh2P particles were formed resulting in low HDS activity. In contrast, the Rh-P/NaBEA catalyst has a three-dimensional micro-pore structure, so the phosphates easily diffused into the micropores and adsorbed on the nearby cation exchange sites. Therefore, since Rh2P formation needed high reduction temperature, the BEA structure might be partially collapsed. In the Rh-P/NaMFI catalyst, well-dispersed Rh2P was formed at relatively low reduction temperature, so the HDS conversion was the highest among the Rh-P/zeolite catalysts.

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References

1) Prins, R., Bussell, M. E., Catal. Lett., 142, 1413 (2012).
2) Oyama, S. T., Gott, T., Zhao, H., Lee, Y.-K., Catal. Today, 143, 94 (2009).
3) Sun, F., Wu, W., Wu, Z., Guo, J., Wei, Z., Yang, Y., Jiang, Z., Tian, F., Li, C., J. Catal., 228, 298 (2004).
4) Oyama, S. T., Lee, Y.-K., J. Catal., 258, 393 (2008).
5) Wang, R., Smith, K. J., Appl. Catal. A: General, 380, 149.

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| Support | W/F [g h/mol] | Reduction temperature [°C] | Conversion [%] | Selectivity [%] | C1-C3<sup>a</sup> | Butanes | Butenes | THT<sup>b</sup> | >C5<sup>c</sup> |
|---------|---------------|----------------------------|----------------|----------------|-----------------|--------|--------|--------|--------|
| NaMOR   | 37.9          | 500                        | 10.2           |                | 2.0             | 3.0    | 66.9   | 28.2   | -      |
| NaMFI   | 4.93          | 600                        | 9.9            |                | 0.8             | 3.1    | 81.4   | 14.7   | -      |
| NaBEA   | 11.48         | 800                        | 9.7            |                | 3.4             | 2.6    | 82.8   | 9.3    | 1.5    |

Table 5 Product Distributions of Thiophene HDS over Reduced Rh-P/zeolite Catalysts

Reaction conditions: catalyst weight = 0.013-0.1 g, H2/C4H4S= 30 and total pressure = 0.1 MPa.

a) C1-C3 hydrocarbons.
b) Tetrahydrothiophene.
c) Polymerized products.

lys reduced at the optimal temperature was evaluated at the same conversion (approximately 10 %). Table 5 shows the product distributions of the Rh-P/zeolite catalysts. The main HDS products of the Rh-P/NaMFI catalyst were butanes, butenes, tetrahydrothiophene (THT) and cracking products (C1-C3). This trend was similar with the HDS products of Rh-P/SiO2 catalyst<sup>13</sup> at the same thiophene conversion (10.4 %). On the other hand, trace amount of 1,3-butadiene was produced over the Rh-P/NaMFI and Rh-P/NaBEA catalysts, and trace amount of 2-methylthiophene was produced over the Rh-P/NaBEA catalyst. The butenes selectivity of the Rh-P/NaMFI catalyst (82.8 %) was equal to that of Rh-P/NaMFI catalyst (81.4 %). However, the butenes selectivity of the Rh-P/NaMOR catalyst was lower (66.9 %). Moreover, the THT selectivity of the Rh-P/NaMOR catalyst was significantly higher (28.2 %) as compared with that of the Rh-P/NaMFI catalyst (14.7 %). The sulfur tolerance of Pd and Pt catalysts decreases with greater particle size<sup>24</sup>. In our study, the Rh-P/ZrO2 catalyst, which had large Rh2P crystallites, exhibited high THT selectivity.<sup>9</sup> The active sites for C-S bond cleavage would be poisoned by H2S<sup>9</sup>. In this study, the Rh-P/NaMOR catalyst showed low sulfur tolerance due to aggregation of Rh2P particles. Therefore, high THT selectivity and low butenes selectivity were observed over the Rh-P/NaMOR catalyst. The C1-C3 selectivity of the Rh-P/NaBEA catalyst was slightly higher (3.4 %), in particular, propylene was mainly obtained, compared with the Rh-P/NaMOR and Rh-P/NaMFI catalysts. Moreover, polymerized products (>C5), which include C5 hydrocarbons, benzene, toluene and xylenes, were also observed over the Rh-P/NaBEA catalyst. The C-S bond in thiophene was cleaved on the active sites to form the ring-opened intermediates. These intermediates react on the acid sites of the support to form methylthiophenes, benzene, toluene and propylene<sup>35</sup>. Slight cumene cracking activity of the NaBEA support was observed (Fig. 1(a)). These results suggest that the formation of >C5 and C1-C3 products over the Rh-P/NaBEA catalyst was due to small amount of acid sites. The THT selectivity of the Rh-P/NaBEA catalyst (9.3 %) was lower than that of the Rh-P/NaMFI catalyst (14.7 %). Presumably thiophene was cleaved to ring-opened intermediates on the acid sites of NaBEA, followed by reaction to form >C5 and C1-C3 products without THT formation.
Na ゼオライト担体上の Rh₂P の生成と水素化脱硫活性

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リン化ロジウム (Rh₂P) の生成、分散性および水素化脱硫 (HDS) 活性に対するゼオライト担体の構造の影響について検討した。TPR より、リン酸種の還元温度の序列は Na-beta > NaMFI > NaMOR であった。XRD の結果から、Rh₂P の生成温度の序列はリン酸種の還元しやすいの序列と一致することがわかった。また、Rh₂P/NaMOR 触媒の CO 吸着量は他の触媒よりも著しく低かった。これより、NaMOR 担体は 1 次元チャネルを有する細孔構造であるため、リン酸種および Rh 種が細孔内へ拡散しにくいことが示唆された。チオフェンの HDS 活性の序列は NaMFI > Na-beta > NaMOR であった。TEM 像から得られた Rh₂P の平均粒子径は NaMOR > Na-beta = NaMFI の序列であった。Na-beta 上では Rh₂P の生成に高温を要したため、崩壊した beta 担体に Rh₂P 粒子が覆われたと推測された。以上より、NaMFI 上では比較的低温で分散性の良い Rh₂P が生成したため、高活性を示したと考えられる。