Hydrodenitrogenation of Pyrrole over Silica-supported Ruthenium Phosphide Catalyst

Yasuharu KANDA†1)*, Toru ARAKI†2), Masatoshi SUGIOKA†3), and Yoshio UEMICHI†1)

†1) Applied Chemistry Research Unit, College of Environmental Technology, Graduate School of Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, JAPAN
†2) Div. of Applied Sciences, Graduate School of Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, JAPAN
†3) Aeronautics and Astronautics Unit, College of Design and Manufacturing Technology, Graduate School of Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran, Hokkaido 050-8585, JAPAN

(Received June 6, 2012)

Catalytic properties of ruthenium phosphide (Ru2P) supported on silica for hydrodenitrogenation (HDN) of pyrrole were compared with those of Ru/SiO2 catalyst to clarify the effect of phosphidation. At higher W/F (652 g h mol⁻¹), pyrrole conversion over Ru/SiO2 catalyst remarkably decreased with increasing reduction temperature. In contrast, pyrrole conversion over P-added Ru (Ru-P/SiO2) catalyst at the same W/F was enhanced with increasing reduction temperature due to Ru2P formation. This activity was higher than that of sulfided NiMoP/Al2O3 catalyst but lower than that of Ru/SiO2 catalyst at the same W/F. At lower W/F (130-391 g h mol⁻¹), Ru-P/SiO2 catalyst showed higher activity and stability for pyrrole HDN than Ru/SiO2 catalyst. The cracking products (almost all CH4) were formed over Ru/SiO2 catalysts and butanes were formed over Ru-P/SiO2 catalysts. The results of CO adsorption and TEM images revealed that the particle size of Ru-P/SiO2 catalyst was smaller than that of Ru/SiO2 catalyst. The TOF of Ru-P/SiO2 catalyst increased with reduction temperature, and this TOF was lower than that of Ru/SiO2 catalyst. After HDN reaction, the peak of particle size distribution for Ru/SiO2 catalyst shifted to larger diameter, whereas that of Ru-P/SiO2 catalyst remained the same. Therefore, the stable activity of Ru-P/SiO2 catalyst can be explained by excess phosphorus species acting to stabilize Ru2P particles.

Keywords
Ruthenium phosphide catalyst, Hydrodenitrogenation, Pyrrole, Deactivation, Particle size

1. Introduction

Hydrodesulfurization (HDS) is one of the most important processes in the petroleum industry for the production of clean fuels to prevent acid rain and deactivation of automotive exhaust catalysts. In this decade, the regulation of sulfur contents of gasoline and diesel fuel in Japan has become significantly more severe. In the near future, regulation of sulfur oxide (SOx) emissions from ships will be tightened, because fuels for ships contain larger amounts of sulfur compounds compared with gasoline and diesel fuel. Therefore, the petroleum industry requires the development of highly active HDS catalysts to produce cleaner fuels.

CoMo/Al2O3 catalysts have been widely used in the HDS process. New active phases, not present in sulfided CoMo catalysts, have received much attention as new HDS catalysts. In particular, many studies have reported that Ni2P catalyst has high potential for HDS. On the other hand, noble metal phosphides (NMxPy), such as rhodium phosphide (Rh2P)9),10) and ruthenium phosphide (Ru2P)9),12),13), supported on SiO2 have high and stable HDS activities. Organic nitrogen compounds are well known to poison HDS catalysts2),14) and ruthenium phosphide catalysts showed higher activity than other noble metal catalysts, such as Rh, Pt, and Re15). These results imply that Ru2P catalyst would show high activity for HDN reaction. The present study examined the catalytic activity of Ru2P catalyst for HDN of pyrrole as compared with Ru catalyst to clarify the effect of phosphidation.

2. Experimental

2.1. Preparation of Catalysts

Silica (SiO2, BET surface area 295 m² g⁻¹) was obtained from Nippon Aerosil Co., Ltd. P-added ruthen-
nium (Ru–P)/SiO2 catalysts were prepared by an impregnation method using aqueous solutions of ruthenium (III) chloride trihydrate (RuCl3·3H2O) and ammonium dihydrogen phosphate (NH4H2PO4). Ru and P loading was 5 and 1.5 mass%, and P/Ru molar ratio was 0.98. Impregnated catalysts were dried at 110 °C for 24 h followed by heat treatment in a nitrogen (N2) stream at 450 °C for 1 h to decompose the salts. The Ru–P catalysts were then pressed into disks and crushed to obtain 30–42 mesh size granules. The sieved catalysts were calcined in air at 500 °C for 4 h. The ramp rate of heat treatment and calcination was 10 °C min⁻¹. Ru/SiO2 catalyst was also prepared by the above procedure using RuCl3·3H2O.

2.2. Hydrodenitrogenation of Pyrrole

HDN of pyrrole was performed at 320 °C under 0.1 MPa using a conventional fixed bed flow reactor. Ru/SiO2 or Ru–P/SiO2 catalyst (0.02-0.1 g) was heated with 10 °C min⁻¹ in a He stream (30 mL min⁻¹) at 500 °C for 1 h. After He treatment, the catalysts were reduced with H2 (30 mL min⁻¹) at 450-700 °C for 1 h. Hydrogen-pyrrole gas mixture (H2/C4H4NH = 523), obtained by passing a H2 stream through a pyrrole trap cooled at 0 °C, was introduced into the reactor. Reaction condition (W/F) was 130-652 g h mol⁻¹. The reaction products were analyzed with gas chromatographs (FID) equipped with Stabilwax DB (15 m, 70-200 °C, 20 °C min⁻¹) and Al2O3/KCl (25 m, 60-190 °C, 6 °C/min) columns, respectively. NiMoP/Al2O3 was used as a reference catalyst. Presulfided NiMoP/Al2O3 catalyst was prepared using 5 vol% H2S-H2 at 400 °C after hydrogen reduction at 450 °C.

2.3. Characterization of Catalysts

SiO2-supported Ru and Ru–P catalysts were characterized by CO adsorption and transmission electron microscopy (TEM) techniques. CO adsorption on Ru/SiO2 and Ru–P/SiO2 catalysts was measured using the pulse method. Ru/SiO2 and Ru–P/SiO2 catalysts (0.1 g) were treated in helium (He) at 500 °C (heating rate: 10 °C min⁻¹) for 1 h, followed by reduction in hydrogen (H2) at 450-700 °C for 1 h. CO was injected onto the catalyst layer at 25 °C using the sampling loop. The amount of CO adsorbed was measured with a Shimadzu GC-8A gas chromatograph (TCD). TEM observation was carried out using a JEOL JEM-2000FX using acceleration voltage 200 kV and magnification 120,000. The particle size distributions of Ru/SiO2 and Ru–P/SiO2 catalysts before and after HDN reaction were obtained by measuring the diameters of more than 1000 particles.

3. Results and Discussion

3.1. HDN of Pyrrole over SiO2-supported Ru and Ru–P Catalysts

3.1.1. Effect of Reduction Temperature on Catalytic Activity for Pyrrole HDN

Figure 1 shows the HDN of pyrrole over SiO2-supported Ru and Ru–P catalysts reduced at various temperatures. Ru/SiO2 catalyst reduced at 450 °C showed stable activity with time on stream. However, pyrrole conversion over Ru/SiO2 catalyst reduced at 650 °C was sharply decreased, whereas pyrrole conversion over Ru–P/SiO2 catalysts slowly decreased. SiO2-supported Ru and Ru–P catalysts showed higher pyrrole conversion than commercial presulfided NiMoP/Al2O3 catalyst. Relationships between reduction temperature and pyrrole conversion over Ru/SiO2 and Ru–P/SiO2 catalysts after reaction for 3 h are shown in Fig. 2. Pyrrole conversion for Ru/SiO2 catalyst decreased with increasing reduction temperature. On the other hand,
the optimal reduction temperature of Ru-P/SiO₂ catalyst was 600 °C. Pyrrole conversion over sulfided NiMoP/Al₂O₃ catalyst is also shown in Fig. 2. Ru/SiO₂ and Ru-P/SiO₂ catalysts showed significantly higher activity than commercial NiMoP/Al₂O₃ catalyst.

Table 1 shows the reaction products for SiO₂-supported Ru and Ru-P catalysts. The main reaction product over Ru/SiO₂ catalyst was cracked hydrocarbons (almost all CH₄). Ru/SiO₂ catalyst reduced at 550 °C showed the same conversion as Ru-P/SiO₂ catalyst reduced at 550-650 °C. In contrast, butanes were formed with higher selectivity over Ru-P/SiO₂ catalysts reduced at 550-650 °C.

In general, higher cracking activity causes greater carbon deposition. Thus, we evaluated the total peak areas of reactant and products detected by FID to estimate carbon deposition on SiO₂-supported Ru and Ru-P catalysts. After HDN reaction, the product gas contains large amounts of carbon atoms related to reactant gas, because hydrogen is consumed by the HDN reaction. Thus, the total peak area of the product gas detected by FID is larger at higher conversion than that at lower conversion. Over Ru/SiO₂ catalyst reduced at 650 °C (Fig. 1(a)), the total peak area was 60,000 at high conversion (100.0 %), compared to 62,000 at low conversion (0.2 %). Such marginal increase of peak area with decreasing conversion implies coke deposition on the Ru/SiO₂ catalyst. The same trend was also observed on Ru-P/SiO₂ catalyst reduced at 700 °C with remarkable deactivation (conversion: from 98.9 to 15.9 %, Fig. 1(b)), total area slightly increased from 60,000 to 61,000. Since the total peak area before deactivation was hardly changed with that after deactivation, the amounts of carbon deposition on Ru/SiO₂ and Ru-P/SiO₂ catalysts are presumably small. Therefore, carbon deposition cannot explain the difference in stability of catalytic activity.

3.1.2. Effect of W/F on Catalytic Activity for Pyrrole HDN

Remarkable deactivation was observed for the Ru/SiO₂ catalyst reduced at 650 °C. However, deactivation rate of the Ru-P/SiO₂ catalysts was slower than that of the Ru/SiO₂ catalysts, as shown in Fig. 1. Thus, Ru-P/SiO₂ catalyst would achieve higher pyrrole conversion than the Ru/SiO₂ catalyst under severe reaction conditions. Figure 3 shows the pyrrole conversion for SiO₂-supported Ru and Ru-P catalysts after 3 h reaction as a function of W/F. For Ru catalyst, the catalytic activity was remarkably reduced with decreasing W/F from 522 to 391 g h mol⁻¹, and significantly low.
pyrrole conversion was observed at W/F from 391 to 130 g h mol⁻¹. Ru/SiO₂ catalysts reduced at 450 °C showed significantly higher activity. On the other hand, Ru/SiO₂ catalysts reduced at higher temperature (600 °C and 650 °C) showed remarkably reduced activities with time on stream, as shown in Fig. 1(a). At lower W/F (below 391 g h mol⁻¹), Ru/SiO₂ catalyst was completely deactivated in a shorter time than 3 h. Thus, the reduced activity of Ru/SiO₂ catalyst with decreasing W/F was caused by significant deactivation within 3 h reaction. On the other hand, HDN conversion for Ru-P catalyst decreased linearly with decreasing W/F. Below W/F 391 g h mol⁻¹, Ru-P/SiO₂ catalyst showed higher pyrrole conversion than Ru/SiO₂ catalyst.

The HDN reaction products over SiO₂-supported Ru and Ru-P catalysts with different W/F are listed in Table 2. For Ru/SiO₂ catalyst, the selectivity for C₁-C₃ hydrocarbons was reduced with decreasing W/F but selectivities for other products increased. For Ru-P/SiO₂ catalyst, the selectivities for C₁-C₃ hydrocarbons and butanes were reduced with decreasing W/F, whereas selectivities increased for organic nitrogen compounds (pyrrolidine and n-butylamine) and others. Other products were observed between pyrrolidine (retention time: 0.60 min) and pyrrole (3.30 min) in the chromatogram of reaction products using Stabilwax DB. Furthermore, the catalysts with higher pyrrole conversion showed lower selectivity for other products.

2-Methylpyrrolidine and 2-methylpyrrole react with pentyamine to form N-alkylated compounds during the HDN of 2-methylpyrrolidine over NiMo/Al₂O₃ catalyst. Other products with high selectivity were observed in the HDN of pyrrole, as shown in Table 1. Under our analysis conditions, the peak of N-methylpyrrole appeared at 1.15 min, which was close to the peak of pyrrolidine compared with pyrrole, indicating that N-alkylated compounds with higher molecular weight, such as N-butylpyrrole, would be observed between N-methylpyrrole and pyrrole, and the selectivity for products observed after N-methylpyrrole was smaller than the selectivity for products observed before N-methylpyrrole. Therefore, other products can be identified as nitrogen compounds, such as pyrrolines (before N-methylpyrrole), N-alkylated products and polymerized products. On the other hand, we previously reported that the selectivity for butanes of Ru-P/SiO₂ catalyst was higher than that of Ru/SiO₂ catalyst, and that 1,3-butadiene was formed over Ru/SiO₂ catalyst. This result implies that Ru-P/SiO₂ catalyst has high hydrogenation activity, and this trend conflicted with the HDN reaction. Sulphidation with carbon disulfide caused remarkable deactivation of metallic Ru catalyst for the HDN reaction. Thus, Ru/SiO₂ catalyst has high hydrogenating activity in the presence of nitrogen compounds, but hydrogenating activity is reduced by poisoning of sulfur compounds. Aromatic nitrogen compounds are denitrogenated after hydrogenation. The selectivities for HDN intermediates, such as other products (include pyrrolines), pyrrolidine and n-butylamine, increased for Ru-P/SiO₂ catalyst with decreasing W/F. However, pyrrolidine and n-butylamine were not formed on Ru/SiO₂ catalyst. Phosphorus in SiO₂-supported Ru₃P and Ru₇P catalysts would enhance Lewis acidity at the surface, and enhanced surface Lewis acidity stabilizes the η¹(O)-intermediate to form C₃ hydrocarbons in the hydrodeoxygenation (HDO) of furan. On the other hand, η²(C, O)-intermediate dominates on Ru/SiO₂ catalyst, and this intermediate would be expected to favor the decarbonylation pathway to yield C₃ products. Therefore, the intermediate formed in the HDN of pyrrole would also decide the selectivities for the products.

3.2 Characterization of SiO₂-supported Rh and Rh-P Catalysts

3.2.1 CO Uptake of SiO₂-supported Ru and Ru-P Catalysts

CO uptake of SiO₂-supported Ru and Ru-P catalysts was examined to estimate the number of active sites. CO is adsorbed in four different modes on reduced and sulfided Ni₃P/SiO₂ catalysts with the following assignments: CO terminally bonded to Ni³⁺ sites; CO ad-
sorbed on Ni$^{\delta+}$ bridge sites; CO terminally bonded to P; and formation of Ni(CO)$_4$\textsuperscript{19). However, CO was desorbed from P by annealing at 27 °C, and P inhibited CO adsorption on Ni bridge sites and formation of Ni(CO)$_4$\textsuperscript{19). If CO is linearly adsorbed on Ru$_2$P as well as Ni$_2$P, the number of Ru sites can be estimated by CO uptake.

Figure 4 shows the CO uptake of SiO$_2$-supported Ru and Ru-P catalysts as a function of reduction temperature. The CO uptake of Ru catalyst hardly changed with increasing reduction temperature. In contrast, the CO uptake of Ru-P/SiO$_2$ catalyst was strongly affected by reduction temperature. The CO uptake of Ru-P/SiO$_2$ catalysts remarkably decreased with increasing reduction temperature from 450 to 550 °C, whereas CO uptake decrease was mitigated at reduction temperatures above 550-600 °C. The X-ray diffraction (XRD) patterns of Ru-P/SiO$_2$ catalysts reduced at 500-650 °C showed that Ru$_2$P was completely formed after reduction above 600 °C\textsuperscript{19). These results indicate that the formation of Ru$_2$P may cause remarkable decrease of CO uptake. However, the CO uptakes of Ru-P/SiO$_2$ catalysts were higher than those of Ru/SiO$_2$ catalysts.

### 3.2.2. TEM Images of SiO$_2$-supported Ru and Ru-P Catalysts

Figure 5 shows the TEM images of Ru/SiO$_2$ and Ru-P/SiO$_2$ catalysts before and after HDN reaction. Before reaction, small Ru and Ru$_2$P particles were observed. The mean diameter of the particles was 14.62 nm for Ru/SiO$_2$ catalyst reduced at 450 °C and 11.53 nm for Ru-P/SiO$_2$ catalyst reduced at 600 °C. These results agreed with the results of CO adsorption,
as shown in Fig. 4. In Pt–Ru bimetallic catalyst, the Pt–Ru bond can be cleaved by P addition\(^{20}\). Therefore, the decrease in particle size may be due to added P causing cleavage of the Ru–Ru bonds to form small Ru-P particles as compared with the Ru/SiO\(_2\) catalyst. Significantly larger Ru particles were observed in Ru/SiO\(_2\) catalyst after HDN reaction. Large Ru-P particles were also observed in Ru-P/SiO\(_2\) catalyst after HDN reaction, but these particles were much smaller than the large particles observed in Ru/SiO\(_2\) catalyst. The mean diameter of particles after HDN reaction was 19.38 nm for Ru/SiO\(_2\) catalyst and 18.59 nm for Ru-P/SiO\(_2\) catalyst.

Figure 6 shows the particle size distributions of Ru/SiO\(_2\) and Ru-P/SiO\(_2\) catalysts before and after HDN reaction. The particle size distribution of Ru/SiO\(_2\) catalyst reduced at 450 °C shifted to larger diameters after HDN reaction. The peak center of the particle size distribution for Ru-P/SiO\(_2\) catalyst after HDN reaction was the same as that before reaction. Phosphate reacts with the hydroxyl group on Al\(_2\)O\(_3\)\(^{22}\). Furthermore, phosphates in Pd-added Ni\(_2\)P catalyst were not completely reduced at 600 °C\(^{21}\). These results indicate that the weak interaction between Ru and SiO\(_2\) support causes remarkable sintering, but excess P species would act to stabilize Ru-P particles.

### 3.2.3. Turnover Frequency of SiO\(_2\)-supported Ru and Ru–P Catalysts for HDN of Pyrrole

Table 3 shows the turnover frequency (TOF) of Ru/SiO\(_2\) and Ru-P/SiO\(_2\) catalysts for HDN of pyrrole. We calculated the TOF using the CO uptake (assuming CO/Ru = 1). The TOF of Ru/SiO\(_2\) catalysts remarkably decreased with increasing reduction temperature. This decrease in TOF can be explained by significant deactivation. In contrast, the TOF of Ru-P/SiO\(_2\) catalyst increased with reduction temperature (except at 700 °C), Ru-P was formed at high reduction temperature (above 600 °C\(^9\)). These results indicate that Ru-P formation enhanced the TOF of Ru-P/SiO\(_2\) catalyst. The TOF of Ru-P/SiO\(_2\) catalyst reduced at 700 °C was lower than that of catalyst reduced at 650 °C. Ru-P was formed at P/Ru = 0.86 and Ru-P was formed at P/Ru = 1.1\(^{12}\). In this study, the P/Ru was 0.98, which is between 0.86 and 1.1. Phosphidation proceeds from the surface into the bulk of the particle\(^{21}\). Therefore, the surface of Ru-P would react with excess P reduced at higher temperature (700 °C) to form Ru-P. Consequently, the formation of Ru-P caused the low TOF of Ru-P/SiO\(_2\) catalyst reduced at 700 °C compared with other reduction temperatures.

The sulfided Ru/C catalyst showed equivalent activity for pyridine HDN to the sulfided NiMo/Al\(_2\)O\(_3\) catalyst\(^{23}\). Ru/SiO\(_2\) and Ru-P/SiO\(_2\) catalysts showed higher activity than NiMo/Al\(_2\)O\(_3\) catalyst, as shown in Figs. 1 and 2. Therefore, these catalysts would show higher activity for HDN than sulfided Ru catalyst. On RuS\(_2\) catalysts, hydrogen adsorbed on S–S anion pairs form sulfhydryl groups and these surfaces provide tetrahydrothiophene (THT) formation\(^{24}\). Furthermore, HDS of thiophene occurs on the corner and edge sites of metallic Ru and hydrogenation of thiophene occurs on

![Fig. 6 Particle Size Distribution of (a) Ru/SiO\(_2\) and (b) Ru-P/SiO\(_2\) Catalysts before and after HDN Reaction](attachment:image.png)

**Table 3** TOF of Supported Ru and Ru-P Catalysts Reduced at Various Temperatures (W/F = 652 g h mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Reduced temp. [°C]</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>199.3</td>
<td>209.8</td>
<td>149.8</td>
<td>98.5</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>Ru-P</td>
<td>16.8</td>
<td>30.2</td>
<td>45.0</td>
<td>48.4</td>
<td>63.9</td>
<td>17.9</td>
</tr>
</tbody>
</table>

a) Calculated from pyrrole conversion at W/F = 522 g h mol\(^{-1}\).

large Ru particles with (S$_2$)$_3^{2-}$ and S$_2^{2-}$ anions$^{25}$. Therefore, HDN of pyrrole would occur on the corner and edge sites of Ru catalyst.

Cracking products were formed on the metallic ensemble in the HDN of pyridine$^{23}$. The reaction product was mainly CH$_4$ over Ru/SiO$_2$ catalyst, as shown in Table 1. On the other hand, butanes were mainly formed over Ru-P/SiO$_2$ catalysts. These results imply that the metallic Ru ensemble would be destroyed by phosphidation. Furthermore, pyrrole hydrogenation over Pt/SBA-15 is structure-insensitive, whereas the ring opening reaction to form n-butylamine is structure-sensitive$^{20}$. The particle size of Ru increased after HDN reaction (Figs. 5 and 6). Moreover, Ru/SiO$_2$ catalyst with low activity produced mainly other products (Table 2). These results imply that the ring opening reaction to form n-butylamine over Ru/SiO$_2$ catalyst was also structure-sensitive.

4. Conclusions

Pyrrole conversion over Ru/SiO$_2$ catalyst at higher W/F (652 g h mol$^{-1}$) remarkably decreased with increasing reduction temperature. In contrast, pyrrole conversion over Ru-P/SiO$_2$ catalyst was enhanced with increasing reduction temperature. This activity was higher than that of sulfided NiMoP/Al$_2$O$_3$ catalyst but lower than that of Ru/SiO$_2$ catalyst at the same W/F. Furthermore, Ru-P/SiO$_2$ catalyst reduced at 700 $^\circ$C showed lower activity than the same catalyst reduced at 650 $^\circ$C. The Ru-P/SiO$_2$ catalyst had higher activity and stability for HDN than Ru/SiO$_2$ catalyst at lower W/F. The results of CO adsorption and TEM images revealed that the particle size of Ru-P/SiO$_2$ catalyst was smaller than that of Ru/SiO$_2$ catalyst. The TOF of Ru-P/SiO$_2$ catalyst increased with reduction temperature but remained lower than that of Ru/SiO$_2$ catalyst. After HDN reaction, the peak of particle size distribution of the Ru/SiO$_2$ catalyst shifted to larger diameter, but remained the same for Ru-P/SiO$_2$ catalyst. Therefore, the stable activity of Ru-P/SiO$_2$ catalyst can be explained by excess phosphorus species acting to stabilize the Ru$_2$P particles.

Acknowledgment

This work was partially supported by a Grant-in-Aid for Young Scientists (B), Japan (21750158). The authors acknowledge Nippon Aerosil Co., Ltd. for supplying the silica gel and Prof. Yasuaki Okamoto (Graduate School of Material Science, University of Hyogo) for helpful discussions.

References


Acknowledgment

This work was partially supported by a Grant-in-Aid for Young Scientists (B), Japan (21750158). The authors acknowledge Nippon Aerosil Co., Ltd. for supplying the silica gel and Prof. Yasuaki Okamoto (Graduate School of Material Science, University of Hyogo) for helpful discussions.

References

要旨

シリカ担持リン化ルテニウム触媒によるビロールの水素化脱窒素反応

神田 康晴1)，荒木 徹2)，杉岡 正敏1)，上道 芳夫1）

1) 室蘭工業大学大学院工学研究科くらし環境系領域応用化学ユニット，050-8585 北海道室蘭市水元町27-1
2) 室蘭工業大学大学院工学研究科応用化学系専攻，050-8585 北海道室蘭市水元町27-1

ビロールの水素化脱窒素反応に対するシリカ担持リン化ルテニウム(Ru2P)の触媒特性について検討し，RuSiO2触媒のHDN特性と比較することでリン化処理の効果を明確にすることを目的とした。W/F=652 g h mol⁻¹では、RuSiO2触媒のビロール転化率は還元温度を上昇させると著しく低下した。一方，同じW/FでのP添加Ru(Ru-P/SiO2)触媒のビロール転化率は還元温度を上昇させると向上し，これはRu2Pの生成によってもたらされた。この活性は硫化処理したNiMoP/Al2O3触媒の活性よりも高かったが，Ru触媒の活性よりも低いことが分かった。W/Fを低下させると，Ru-P/SiO2触媒はRu触媒よりも高く，安定な活性を示すことが分かった。また，Ru/SiO2触媒上ではクラッキング生成物（大部分がCH₄）が得られ，Ru-P/SiO2触媒上では主にプロトンが生成した。CO吸着およびTEMの結果から，Ru-P/SiO2触媒の粒子径はRu触媒よりも小さいことが明らかとなった。Ru-P/SiO2触媒のTOFは還元温度の上昇により向上したが，Ru/SiO2触媒のTOFよりも低下した。Ru/SiO2触媒の粒径分布のピークは，HDN反応を行うと粒径が大きい方にシフトするのに対し，Ru-P/SiO2触媒の粒径分布はHDN反応後でもピークのシフトは見られなかった。以上的ことから，Ru-P/SiO2触媒がRu/SiO2触媒よりも安定な活性を示したのは，過剰なリンがアンカーとして働くことでRu₂P粒子の凝集を防ぐことができたためと推測される。