Hydrogenation Ability of ZSM-5 Zeolite

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Hydrogenation of ethylene and propylene was carried out over the protonated ZSM-5 (HZSM-5) and the alkaline earth metal-containing ZSM-5 type zeolites (M-HZSM-5, M: alkaline earth metal). Products, both of low and high molecular weights, were formed through a variety of reactions such as polymerization, isomerization, cracking, and hydrogenation. The lower molecular weight hydrocarbons produced over the HZSM-5 were mainly paraffins. The yields of light olefins were dependent on the kinds of zeolite used and increased in the following order: HZSM-5=Mg-HZSM-5<Ca-HZSM-5<Sr-HZSM-5<Ba-HZSM-5. Hydroconversion of benzene was also carried out over these zeolites. The catalytic activity of M-HZSM-5 was lower than that of HZSM-5. In the case of M-HZSM-5, the hydrogenated product, cyclohexane, and its skeleton isomer, methylocyclopentane, were detected in the reaction products at about 300°C. In order to clarify the essential sites for the hydrogenation, effects of impurities, especially iron, contained in the zeolites as hydrogenation catalysts, were studied in detail. It was found that the HZSM-5 zeolite, which does not contain iron at all, showed a significant hydrogenation activity. From these results, we have concluded that the active sites for the hydrogenation of ethylenic double bonds are the strong acid sites of the HZSM-5 zeolite, and that the hydrogenation activity decreases upon the modification of the zeolite with alkaline earth metals.

1. Introduction

Zeolites containing catalysts have been used in numerous petrochemical reactions such as cracking, alkylation, oligomerization, isomerization, and disproportionation due to their shape-selective characteristics, acidic natures and well-defined structures. However, relatively little information on the hydrogenation ability of zeolites is available. It is very important for the design of zeolite catalysts to know if the zeolite alone has the hydrogenation ability. In this paper, the hydrogenation ability of the protonated ZSM-5 zeolite is described.

2. Hydrogenation of Light Olefins

The conversion of synthesis gas to hydrocarbons in a two-stage system consisting of a methanol synthesis reactor containing Zn-Cr oxide (Zn/Cr=2) catalyst followed by a hydrocarbon-forming reactor containing the protonated ZSM-5 zeolite (HZSM-5, Si/Al=120) was carried out. The results obtained are shown in Fig. 1. The C₂ and C₃ hydrocarbons produced were mainly paraffins when the pressure of the second reactor (the hydrocarbon-forming reactor) was above 20 kg/cm². As this fixed-bed unit is a two-stage system, it is reasonable to consider that the C₂ and C₃ paraffins are produced on the HZSM-5 zeolite. There is no doubt that the light olefins are produced as intermediate products and converted to higher hydrocarbons through a variety of reaction steps in the conversion of methanol to hydrocarbons over the zeolite. It is also well

Fig. 1 Synthesis of Light Olefins from Synthesis Gas in Two-stage System

Reaction conditions:
First reactor (Zn-Cr oxides): P=40 kg/cm², SV=1,000 h⁻¹, T=300°C, CO/H₂/Ar=30/60/10.
Second reactor (HZSM-5): SV=5,000 h⁻¹. ○, ○, ○: T=500°C. □, ■, ■: T=400°C.
known that the hydrogen transfer reaction to light olefins takes place on solid-acid catalysts. Therefore, the following two possibilities can be considered for the production of light paraffins; (1) the hydrogen transfer reaction to light olefins over the HZSM-5, (2) the subsequent hydrogenation of light olefins over the HZSM-5.

From these viewpoints, two kinds of mixed gases, C_2H_4-H_2 and C_2H_4-He, were passed over the HZSM-5 zeolites. The results obtained are illustrated in Fig. 2. In the case of the C_2H_4-H_2 system, the C_2H_6 yield increased remarkably by raising the reaction temperature; about 95% of C_2H_4 was converted to C_2H_6 at 545°C. On the other hand, in the case of the C_2H_4-He system, the C_2H_6 yield increased slightly; only about 10% of C_2H_4 was converted to C_2H_6 at 550°C. Therefore, it seems that most of the C_2H_6 obtained in the C_2H_4-H_2 system is produced by hydrogenation of C_2H_4. Moreover, in order to investigate the effect of impurities contained in the HZSM-5, the zeolites before and after C_2H_4-H_2 reaction were carefully analyzed. First, the zeolites were treated with a mixture of sulfuric and nitric acids (H_2SO_4/HNO_3=1/1, vol/vol) to dissolve the impurities. As a result, no metal impurities were detected. Second, the zeolites were completely dissolved with hydrofluoric acid to determine the amounts of impurities contained in them. Only a trace amount of Fe was detected. Other metals were far below the detection limits of the Shimadzu ICP-50 inductively coupled argon plasma emission spectroscope. The amounts of Fe detected in the zeolite before and after the reaction were 0.0065 wt% and 0.0072 wt%, respectively, so that it may be neglected completely in comparison with the amount of Al. These results indicate strongly that the hydrogenation of light olefins takes place on the acidic sites of the HZSM-5.

In order to further clarify the essential sites for the hydrogenation, the following experiments were conducted. Iron-containing silicalite and ZSM-5 type zeolites were prepared from an Fe(II) compound or from Fe(II) and Al compounds. The BET surface area of these iron-containing zeolites was about 350 m^2/g. Peaks corresponding to iron oxide were not observed in the X-ray powder diffraction pattern. Fe(II) did not replace a portion of the silicon atoms in the crystal lattice and was present in an enveloped form with the zeolite. Therefore, the iron-containing silicalite had no acidic nature. On the other hand, the iron-containing ZSM-5 type zeolite had the acidic nature derived from Al when the zeolite was protonated in hydrochloric acid solution. The amount of Fe in the silicalite was 2.18 wt%. In the HZSM-5, the atomic ratio of Si/Al and the amount of Fe were 20 and 0.815 wt%, respectively. Hydrogenation of CO was carried out over these iron-containing zeolites at 300–450°C, as they were inactivated above 450°C. A large difference in the product distribution was observed between the two zeolites (Fig. 3). The C_2 and C_3 hydrocarbons produced over the iron-containing silicalite were mainly olefins, and those produced over the iron-containing HZSM-5 were mainly paraffins, though a small difference in the (C_2H_4+C_2H_6+C_3H_6+C_3H_8) selectivity of both zeolites was observed.

Based on all above results, it is concluded that the hydrogenation of light olefins takes place on
the HZSM-5 zeolite, i.e., the acidic sites of the zeolite.

3. Depression of Hydrogenation Activity by Alkaline Earth Metals

In order to clarify the relationship between hydrogenation activity and acid properties of zeolite, the hydrogenation of ethylene and propylene was carried out over various ZSM-5 type zeolites containing alkaline earth metals (M–HZSM-5, M: alkaline earth metal) (Table 1). We have previously reported that part of the alkaline earth metals changes the strong acid sites of HZSM-5 to weak ones\(^6,7\). \textbf{Figure 4} shows some typical results of the hydrogenation\(^8\). The shaded parts in \textbf{Fig. 4} indicate \(C_2\) to \(C_6\) olefins. Products, both of low and high molecular weights, were formed through a variety of reactions such as polymerization, isomerization, cracking, and hydrogenation. The yields of light olefins and higher carbon-number hydrocarbons (\(C_6^+\)) increased in the following order: HZSM-5=Mg–HZSM-5<Ca–HZSM-5<Sr–HZSM-5<Ba–HZSM-5. In the case of the \(C_2H_4(C_3H_6)–H_2\) system over these alkaline earth metal-containing zeolites, aromatic hydrocarbons (BTX) were hardly obtained as compared with those in the \(C_2H_4(C_3H_6)–He\) system over HZSM-5 (self-hydrogenation). These results indicate that the hydrogenation activity of HZSM-5 is depressed by modification with alkaline earth metals. The increase in the \(C_6^+\) yields over the zeolites modified with alkaline earth metals may be attributable to the occurrence of other reactions such as polymerization, isomerization, and cracking, that take place in preference to hydrogenation.

The temperature programmed desorption (TPD) spectra of NH\(_3\) for HZSM–5 zeolite exhibited two peaks whose maximum temperatures were about 170 and 450°C. By addition of alkaline earth metals, the amount of desorbed NH\(_3\) above 350°C, which corresponded to that of the second peak, for various zeolites decreased in the following order: HZSM–5>Ca–HZSM–5>Mg–HZSM–5>Sr–HZSM–5>Ba–HZSM–5. In \textbf{Fig. 5} are plotted the molar ratios of the \(C_2\) to \(C_5\) paraffins (\(C_2^-\) to \(C_5^-\)) to the \(C_2\) to \(C_5\) olefins (\(C_2^\equiv\) to \(C_5^\equiv\)) over these zeolites (given in \textbf{Fig. 4}) against the normalized amount of desorbed NH\(_3\) based on that of HZSM-5, \(NH_3/NH_3(HZSM-5)\), where \(NH_3\) and \(NH_3(HZSM-5)\) are the amounts of desorbed NH\(_3\) above 350°C for M–HZSM–5 and HZSM–5, respectively\(^8\). Except for Mg–HZSM–5, the \((C_2^-\rightarrow C_5^-)/(C_2^\equiv\rightarrow C_5^\equiv)\) molar ratio decreased as the amount of desorbed NH\(_3\) decreased, namely, the basicity of alkaline earth metal increased.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Cat. No. & Atomic ratios & BET surface area [m\(^2\)/g] \\
\hline
\hline
1. HZSM-5 & 120 & - & 342 \\
2. Mg–HZSM-5 & 395 & - & 356 \\
3. Ca–HZSM-5 & 94 & 1.30 & 336 \\
4. Sr–HZSM-5 & 117 & 1.63 & 341 \\
5. Ba–HZSM-5 & 93 & 1.29 & 301 \\
6. Si–HZSM-5 & 90 & 1.35 & 301 \\
7. Silicalite & - & - & 345 \\
\hline
\end{tabular}
\end{table}
From these results, it is concluded that the hydrogenation of olefins takes place on the strong acid sites of HZSM-5 and that the hydrogenation activity is depressed by modification with alkaline earth metals. Therefore, it is expected that the selectivity of light olefins in the conversion of synthesis gas to hydrocarbons over the dual-functional catalyst, Zn-Cr oxide catalyst and the protonated zeolite, increases by such a modification of the zeolite. The conversion of synthesis gas to hydrocarbons in a two-stage system was carried out using various M-HZSM-5. Figure 6 shows the typical results. The C2 and C3 hydrocarbons produced over HZSM-5 are mainly paraffins. As we would expect, by modifying the HZSM-5 with alkaline earth metals, the (C2H4+C3H6) selectivity increased in the order: HZSM-5 (Si/Al=120)=Mg-HZSM-5<HZSM-5 (Si/Al=395)<Ca-HZSM-5<Sr-HZSM-5<Ba-HZSM-5. On the other hand, the (C2H4+C2H6+C3H6+C3H8) selectivity was hardly depended upon the kinds of zeolites.

4. Hydroconversion of Benzene

As described above, the HZSM-5 zeolite is active for olefin hydrogenation. It is expected that HZSM-5 zeolite alone is also effective for hydroconversion of aromatic hydrocarbons. The hydroconversion of benzene was carried out over various HZSM-5 zeolites, which had SiO2/Al2O3 ratios of 30–240. Typical results obtained are shown in Figs. 7(A) and (B). The amounts of aluminium in the zeolites (Al/(Si+Al)) affected both the conversion of benzene and yields of products. The conversions of benzene increased markedly with increasing amount of aluminium. The products obtained were methane, ethane, propane, and alkylbenzenes (toluene, xylenes). A remarkable increase in the yields of methane and ethane was observed with increasing amount of aluminium. The yield of toluene also increased with the amount of aluminium only in the region of low benzene conversion. However, the yield of toluene instead decreased after attaining a maximum yield of about 15%, as the amount of benzene present to form toluene by alkylation largely decreased. Since the increase in the Al/(Si+Al) ratio corresponds to that in conversion, i.e., catalyst contact time, the presence of a maximum yield of toluene can well be understood.

The amounts of hydrogen incorporated into the products were calculated from the product yields.
Against the amount of aluminium was plotted the normalized amount of hydrogen based on carbon, [(H/C)\textsubscript{p}-(H/C)\textsubscript{r}], where (H/C)\textsubscript{p} and (H/C)\textsubscript{r} are ratios of hydrogen and carbon atoms in the hydrocarbons in the effluent and the feed, respectively. The only hydrocarbon in the feed is benzene, so that (H/C)\textsubscript{r} is 1. As shown in Fig. 7 (B), a remarkable increase in [(H/C)\textsubscript{p}-1] was observed with an increase in the amount of aluminium\textsuperscript{11)}. These results suggest that the hydroconversion comprising hydrogenation of benzene, hydrocracking, and alkylation occurs at the acidic sites of HZSM-5 zeolite.

The amounts of deposited carbon in the zeolites after reaction (15 h) were less than ~1%, so that the amount of hydrogen from benzene found in the conversion products is almost negligible in comparison with the total amount of hydrogen in these products. Therefore, it is not considered that the hydrogenated hydrocarbons are mostly produced by a hydrogen transfer reaction.

However, it is difficult to rule out that small amounts of impurities, especially iron, in the zeolites are the active sites. In order to determine the effect of iron in the zeolite as a hydrogenation catalyst, various iron-containing ZSM-5 type zeolites were synthesized hydrothermally in the presence of an iron compound (FeSO\textsubscript{4}). We have previously reported that Fe(III) can replace a portion of the silicon atoms in a zeolite lattice and give Br\"{o}nsted acidity\textsuperscript{5)}, whereas Fe(II) cannot replace a portion of the silicon atoms and give Br\"{o}nsted acidity. Some analytical data are listed in Table 2. The results of the hydroconversion of benzene carried out using the iron-containing zeolites are illustrated in Fig. 8\textsuperscript{11}). Although Fig. 8 (A) shows scattered results, the conversion of benzene seem to be constant, being independent of the amount of iron. On the other hand, a remarkable change in the yields of products was observed. The yields of ethane and propane increased with the amount of iron, while that of toluene decreased. The [(H/C)\textsubscript{p}-1] indicates the rate of hydrogenation, increased slightly. It is the most striking when the line [(H/C)\textsubscript{p}-1] vs. Fe wt% is extrapolated to 0 wt% Fe, the intercept indicates the significant hydrogenation activity of the zeolite which does not contain iron at all.

Figure 9 shows the results of the hydroconversion of benzene over various M–HZSM–5 zeolites\textsuperscript{10). The catalytic activity of M–HZSM–5 was lower than that of the HZSM–5 and decreased with the amount of alkaline earth metal. The hydrogenated product, cyclohexane, and its skeleton isomer, methylcyclopentane, were detected in the effluent gas at a low reaction temperature of 300°C. These results indicate strongly the occurrence of hydro-

\begin{table}
\centering
\caption{Characteristics of Various Iron-containing HZSM–5 Zeolites}
\begin{tabular}{cccc}
\hline
Cat. & Si/Al & BET surface area & Amount of Fe \\
No. & & [m\textsuperscript{2}/g] & [wt%] \\
\hline
8. & 35 & 340 & 0.0093 \\
9. & 35 & 349 & 0.021 \\
10. & 35 & 357 & 0.102 \\
11. & 35 & 358 & 0.205 \\
12. & 36 & 358 & 0.483 \\
13. & 36 & 357 & 0.599 \\
14. & 38 & 360 & 0.693 \\
\hline
\end{tabular}
\end{table}
Fig. 8 Hydroconversion of Benzene over Various Iron-containing HZSM-5 Zeolites

Reaction conditions: $P=40$ kg/cm$^2$, $T=573$ $\degree$C, SV=5,000 h$^{-1}$, $C_6H_6/H_2=3/97$.

- CH$_4$, C$_2$H$_6$, C$_3$H$_8$, toluene, xylenes.

![Graph showing conversion vs amount of Fe](image)

Reaction conditions: $P=40$ kg/cm$^2$, $T=573$ $\degree$C, SV=5,000 h$^{-1}$, $C_6H_6/H_2=3/97$.

Fig. 9 Hydroconversion of Benzene over ZSM-5 Type Zeolites Modified with Various Alkaline Earth Metals

![Graph showing conversion vs alkaline earth metal/Al](image)

Fig. 10 Hydrocracking of Cyclohexane over HZSM-5 and Ba-HZSM-5

![Graph showing conversion vs temperature](image)

Table 3 Product Distribution for Hydrocracking of Cyclohexane

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cyclohexane conv. [%]</th>
<th>C$_1$</th>
<th>C$_2$</th>
<th>C$_3$</th>
<th>Selectivity [C$_6$-%]</th>
<th>C$_4$</th>
<th>C$_5$</th>
<th>B</th>
<th>T</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>100</td>
<td>48.4</td>
<td>50.0</td>
<td>0.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.6</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Ba-HZSM-5</td>
<td>100</td>
<td>41.9</td>
<td>49.9</td>
<td>3.9</td>
<td>0</td>
<td>0</td>
<td>1.8</td>
<td>1.9</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>HZSM-5$^a$</td>
<td>58.7</td>
<td>11.4</td>
<td>30.5</td>
<td>20.8</td>
<td>7.5</td>
<td>4.4</td>
<td>16.0</td>
<td>7.5</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>HZSM-5$^b$</td>
<td>(95.4)$^b$</td>
<td>45.8</td>
<td>46.8</td>
<td>0.7</td>
<td>0</td>
<td>0</td>
<td>4.8</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Reaction conditions: $P=40$ kg/cm$^2$, $T=573$ $\degree$C, SV=5,000 h$^{-1}$, $C_6H_6/H_2=3/97$.

b) The reaction was carried out using mixed gas of $C_6H_6$ and He instead of mixed gas of $C_6H_6$ and $H_2$.

c) Hydroconversion of benzene was carried out.

d) Olefin fraction.

e) Benzene conversion.
cracking through the hydrogenation of benzene on the strong acid sites of the zeolite. Moreover, the hydrotreatment of cyclohexane was carried out over HZSM-5 (Si/Al=20) and Ba–HZSM-5 (Si/Al=20, Ba/Al=0.075) (Fig. 10, Table 3)10). The conversion of cyclohexane over these zeolites was 100% at reaction temperatures above 360°C. The product distribution over these zeolites was similar to that resulting from the hydroconversion of benzene over HZSM-5 and was considerably different from that resulting from the benzene–He system.

From all above results, we concluded that the active sites for the hydrogenation were the strong acid sites of HZSM-5 and proposed the following reaction scheme (A).

![Reaction Scheme (A)](image)

It is known that the equilibrium constant of the hydrogenation of benzene at high temperatures above 450°C is very small (<10^-6), namely, the equilibrium lies far to the left. Therefore, if the hydroconversion of benzene proceeds by the following reaction scheme(B) in which the rate-determining step is the hydrotreatment of cyclohexane, it is difficult to rule out completely that the hydrogenation of benzene takes place on the impurities contained in the zeolite.

![Reaction Scheme (B)](image)

So, a brief kinetic study was carried out to check the possibility of the reaction scheme(B). As shown in Fig. 11, it is found that the rate of the hydroconversion (r) is first-order dependent on the pressure of benzene, as is expressed by the following Eq. (1).

\[ r = -\frac{dP_b}{dt} = k_h P_b \]  

where \( P_b \) is the partial pressure of benzene, \( t \) is the catalyst contact time and \( k_h \) is an apparent rate constant. Integrating Eq. (1), we have

\[ \ln \left( \frac{P_b}{P_b^0} \right) = -k_h t \]  

where \( P_b^0 \) is the initial partial pressure of benzene in the mixed gas of \( C_6H_6 \) and \( H_2 \). The apparent rate constants at various reaction temperatures were calculated from the straight lines, and they were

\[
\begin{align*}
k_h(480°C) &= 0.596\times10^3 \text{ (1/h)} \\
k_h(510°C) &= 1.55\times10^3 \text{ (1/h)} \\
k_h(541°C) &= 4.64\times10^3 \text{ (1/h)} \\
k_h(573°C) &= 8.72\times10^3 \text{ (1/h)}
\end{align*}
\]

From the Arrhenius plots of \( k_h \) obtained, the apparent activation energy (\( \Delta E_a \)) was 34.8 kcal/mol (Fig. 12).

Then, the "true" activation energy for reaction scheme(B) was calculated by using the apparent activation energy (\( \Delta E_a \)) obtained. \( K \) is an equilibrium constant of the hydrogenation of benzene and is expressed by the following Eqs. (3) and (4).

![Arrhenius Plot of \( k_h \)](image)

\[ K = \frac{P_b}{P_0b} \]

\[ \Delta E_a = 34.8 \text{ kcal/mol} \]
where $P_C$ and $P_H$ are the partial pressures of cyclohexane and hydrogen, respectively. Therefore, the rate of the hydroconversion of benzene for reaction scheme (B) is expressed by using Eq. (4) as follows.

$$r = -\frac{dP_H}{dt} = kP_C = kKPBPH_3$$

where $k$ is a rate constant of the hydrocracking of cyclohexane. $K$ and $k$ are also expressed by the following Eqs. (6) and (7).

$$K = e^{-\frac{\Delta F}{K_T}}$$

$$k = k_0e^{-\frac{\Delta E}{RT}}$$

where $\Delta F$ is the free energy of the hydrogenation of benzene and $\Delta E$ is the activation energy of the hydrocracking of cyclohexane.

$$\ln(kK) = k_0e^{-\frac{\Delta E}{RT}}e^{-\frac{\Delta F}{RT}} = k_0e^{-\frac{\Delta E}{RT} - \frac{\Delta H - T\Delta S}{RT}}$$

where $\Delta H$ is the enthalpy of the hydrogenation of benzene. Therefore,

$$\Delta E_a = 34.8 \text{ kcal/mol} = \Delta E + \Delta H$$

As $\Delta H$ is approximately $-49.3 \text{ kcal/mol}$,

$$\Delta E = 84.1 \text{ kcal/mol}$$

As it is generally reported that the activation energy of cracking is $20-35 \text{ kcal/mol}$, the activation energy ($\Delta E = 84.1 \text{ kcal/mol}$) obtained is considerably larger than those values above. Therefore, it can be concluded that the possibility of reaction scheme (B) is low and that the iron contained in the HZSM-5 is not the essential site for the hydrogenation of benzene.

5. Conclusion

It has been found that the strong acid sites of HZSM-5 zeolite exhibit the significant hydrogenation activity for ethylenic double bonds, and their hydrogenation activity is depressed by modification with alkaline earth metals. The detailed mechanism of the hydrogenation cannot be clarified at the present time. Several investigators have reported that alumina, silica-alumina gels, and crystalline aluminosilicates (mordenite) as solid acids also show such hydrogenation activity and suggested that the active sites for the hydrogenation are the Lewis acid sites in the zeolite.

We expect that new reactions and catalysts will be developed in the near future by utilizing the hydrogenation or the reduction ability of the HZSM-5 zeolite.

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References

要旨

ZSM-5 ゼオライトの水素化能

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プロトン交換した ZSM-5（HZSM-5）およびアルカリ土類金属含有 ZSM-5 型ゼオライト（M-HZSM-5、M：アルカリ土類金属）上でエチレンおよびプロピレンの水素化を行った。重合、異性化、クラッキング、水素化等の反応が併発するため、生成物は低分子量のものから高分子量のものまで生成した。HZSM-5 上で生成する低分子量のものは主にパラフィンであった。低級オレフィンの収率は用いるゼオライトの種類に依存し、次の順に増加した。HZSM-5=Mg-HZSM-5<Ca-HZSM-5<Sr-HZSM-5<Ba-HZSM-5。ベンゼンの水素化分解もこれらのゼオライト上で行った。M-HZSM-5 の触媒活性は HZSM-5 よりも低かった。M-HZSM-5 では、反応温度約300℃で反応生成物中に水素化生成物であるシクロヘキサンとその骨格異性体であるメチルシクロペンタンが検出された。水素化の活性点を明確にするため、ゼオライト中に含まれる不純物、特に鉄の水素化触媒としての効果を詳細に検討した。その結果、鉄を全く含まない HZSM-5 ゼオライトが相当な水素化活性を示すことが明らかとなった。以上の結果から、炭素-炭素二重結合の水素化の活性点は HZSM-5 ゼオライトの強酸点であり、その水素化活性はアルカリ土類金属塩類により抑制されると結論した。

Keywords
ZSM-5, Alkaline earth metal, Hydrogenation, Hydroconversion, Olefin

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