

Olefin Hydrogenation over Zeolite H-ZSM-5

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Conversion of synthesis gas to hydrocarbons was carried out in a two-stage system consisting of a methanol synthesis reactor followed by a hydrocarbon-forming reactor containing H-ZSM-5 zeolite. It was found that the H-ZSM-5 zeolite catalyst was active in olefin hydrogenation.

Many patents and publications claim the direct synthesis of aromatic hydrocarbons and light paraffins from synthesis gas with dual functional catalysts, which are composed of metal oxides (methanol synthesis) and acidic (zeolite) components.^{1)~6)} It has been considered that light paraffins are produced via the subsequent hydrogenation of light olefins as intermediate products over the methanol synthesis catalyst. There have been few reports regarding the direct synthesis of light olefins over such catalysts.

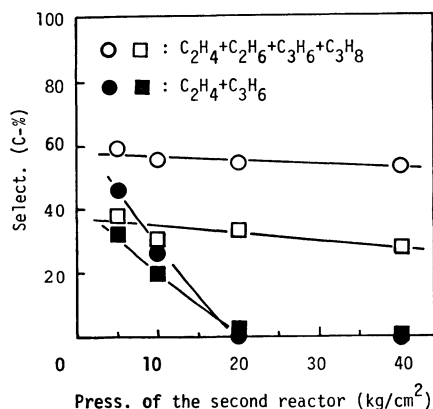
Recently, we have also studied the direct synthesis of light olefins from synthesis gas under various reaction conditions with different dual-functional catalysts^{7)~9)} and have suggested that the possibility of the olefin hydrogenation on H-ZSM-5 zeolite is present in the above direct synthesis of hydrocarbons. In order to clarify this possibility, conversion of synthesis gas was carried out in a two-stage system. In this paper, it is shown that the hydrogenation of olefins takes place over the protonated ZSM-5 zeolite.

ZSM-5 zeolite was synthesized by a method similar to that described in Mobil's patent¹⁰⁾. The atomic ratio of Si to Al in the zeolite was 120. It was protonated in hydrochloric acid solution (1N) and calcined in air at 500°C for 6 h. Zn-Cr oxides catalyst was prepared according to the method reported by Ogino et al. using chromic acid aqueous solution and zinc oxide powder.¹¹⁾ The atomic ratio of Zn to Cr was 2. The reaction was carried out in a high-pressure fixed bed flow system. The catalyst was packed into a quartz tube reactor, which was set in the pressure vessel. The reaction

gas was passed through beds of activated carbon and molecular sieve 5A. All transfer lines were kept at about 150°C by heating tapes to prevent condensation of the reaction products. The effluent gas was directly fed to sampling valves of a Yanaco AG-1000TFH auto gas chromatograph for analysis. Carbon monoxide conversion and carbon-based selectivity (excluding CO₂) were calculated by using argon as an internal standard⁹⁾.

When the reaction was carried out over the Zn-Cr oxides catalyst at 300°C and at a space velocity (SV) of 1,000 h⁻¹ under a pressure of 40 kg/cm², the reaction products were methanol and a trace amount of methane with a CO conversion of about 9%. **Figure 1** shows the results of the conversion of synthesis gas to hydrocarbons in a two-stage system consisting of a methanol synthesis reactor followed by the hydrocarbon-forming reactor containing the H-ZSM-5 zeolite. The reaction conditions of the first reactor (the methanol synthesis reactor) were the same as those described above. On the other hand, the reaction conditions of the second reactor (the hydrocarbon-forming reactor) were at 300~500°C and at SV of 5,000 h⁻¹ under pressures of 5~40 kg/cm². The reaction products on this catalyst system were hydrocarbons, and neither methanol nor dimethyl ether were detected. The C₂ and C₃ hydrocarbons produced were mainly paraffins, when the pressure of the second reactor was above 20 kg/cm². This fixed-bed unit is the two-stage system, so that the C₂ and C₃ paraffins are produced on the H-ZSM-5 zeolite. There is no doubt that the light olefins are produced as intermediate products and upgraded to higher hydrocarbons through a variety of reaction steps in

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Reaction conditions:

the first reactor (Zn-Cr oxides)

$P=40 \text{ kg/cm}^2$, $SV=1,000 \text{ h}^{-1}$, $T=300^\circ\text{C}$

the second reactor (H-ZSM-5)

$SV=5,000 \text{ h}^{-1}$

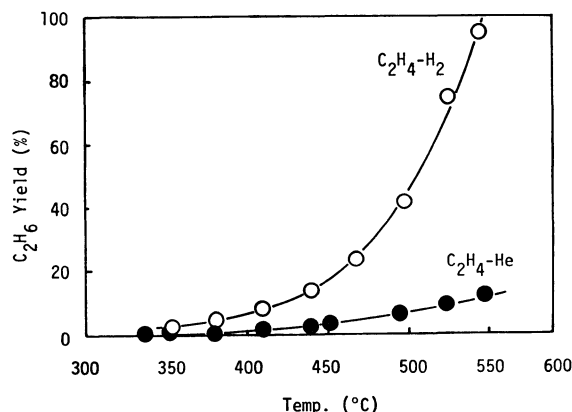
○ ●: $T=500^\circ\text{C}$, □ ■: $T=400^\circ\text{C}$

The reaction gas was composed of 30 mol% CO, 60 mol% H_2 and 10 mol% Ar as an internal standard for analysis.

Fig. 1 Results of the Direct Conversion of Synthesis Gas to Hydrocarbons in a Two-stage System

the conversion of methanol to hydrocarbons over the zeolite. It is also well 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 H-ZSM-5 zeolite, (2) the subsequent hydrogenation of light olefins over the H-ZSM-5 zeolite.

From these viewpoints, two kinds of mixed gases, $\text{C}_2\text{H}_4\text{-H}_2$ and $\text{C}_2\text{H}_4\text{-He}$, were passed over the H-ZSM-5 zeolite catalyst. The results obtained are illustrated in Fig. 2. In case of the $\text{C}_2\text{H}_4\text{-H}_2$ 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 case of the $\text{C}_2\text{H}_4\text{-He}$ 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 C_2H_6 obtained in the $\text{C}_2\text{H}_4\text{-H}_2$ system is produced by the hydrogenation of C_2H_4 . Moreover, in order to investigate the effect of impurities contained in the H-ZSM-5 zeolite, the catalysts before and after the $\text{C}_2\text{H}_4\text{-H}_2$ reaction were carefully analyzed by X-ray fluorescence spectrometry and inductively coupled argon plasma emission spectrometry. Only a trace amount of Fe was detected in the catalyst. The other metals were far below the detection limit of the Shimadzu ICPS-50 inductively coupled argon plasma emission spectroscope. The amount of Fe detected in the



Reaction conditions: $P=40 \text{ kg/cm}^2$, $SV=5,000 \text{ h}^{-1}$

The reaction gas was composed of 2.5 mol% C_2H_4 , 50 mol% H_2 (or He) and 47.5 mol% Ar.

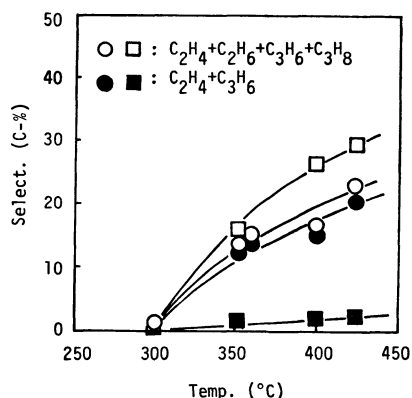
$$\text{C}_2\text{H}_6 \text{ Yield} = \frac{[\text{C}_2\text{H}_6]/[\text{Ar}]}{[\text{C}_2\text{H}_4]_0/[\text{Ar}]_0} \times 100$$

$[\text{C}_2\text{H}_6]$, $[\text{Ar}]$: the concentration in the effluent gas
 $[\text{C}_2\text{H}_4]_0$, $[\text{Ar}]_0$: the initial concentration in the reaction gas

Fig. 2 Results of $\text{C}_2\text{H}_4\text{-H}_2$ and $\text{C}_2\text{H}_4\text{-He}$ Reactions over H-ZSM-5 Zeolite Catalyst

catalyst before and after the $\text{C}_2\text{H}_4\text{-H}_2$ reaction were 0.0065 wt% and 0.0072 wt%, respectively, so that it may be neglected completely in comparison with the amount of Al.

From these results, it is considered that the hydrogenation of C_2H_4 takes place on the H-ZSM-5 zeolite, i.e. the acidic sites of the H-ZSM-5 zeolite. This concept can be supported by the following fact. The modified crystalline silicas were prepared from an Fe(II) compound or Fe(II) and Al compounds⁸). These iron-modified crystalline silicas with BET surface area of about $350 \text{ m}^2/\text{g}$ had a well defined crystalline ZSM-5 type structure, as demonstrated by X-ray diffraction patterns and scanning electron micrographs. Fe(II) did not replace a portion of the silicon atoms in the crystal lattice and was present in an enveloped form with the crystalline silica. Therefore, the catalyst prepared from the Fe(II) compound had no acidic nature. On the other hand, the catalyst prepared from Fe(II) and Al compounds had the acidic nature derived from Al, when the catalyst was protonated in hydrochloric acid solution. Hydrogenation of CO was carried out over these catalysts at $300\sim 450^\circ\text{C}$, as they were inactivated above 450°C . The typical results are shown in Fig. 3. The reaction products of the catalyst prepared from the Fe(II) compound were mainly olefins and those of the catalyst prepared from Fe(II) and Al compounds were mainly paraffins, though small differences in the $(\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8)$ selectivity of both



Reaction conditions : $P=10 \text{ kg/cm}^2$, $SV=1,000 \text{ h}^{-1}$
 The reaction gas was composed of 45 mol% CO , 45 mol% H_2 and 10 mol% Ar .
 ○ ● : the catalyst prepared from an Fe(II) compound
 □ ■ : the protonated catalyst prepared from Fe(II) and Al compounds.

Fig. 3 Results of CO Hydrogenation over Iron-modified Crystalline Silica Catalysts

catalysts were observed. Moreover, the amount of Fe in the catalyst prepared from the Fe(II) compound was 2.18 wt%. In the protonated catalyst prepared from Fe(II) and Al compounds, the atomic ratio of Si to Al and the amount of Fe were 20 and 0.815 wt%, respectively.

From the above results, it was concluded that the H-ZSM-5 zeolite catalyst is active in olefin hydrogenation. Recently, Anthony et al. found that when the mixture of C_2H_4 and H_2 in the ratio of 1 : 1.86 was contacted with Zeolon-500 at 392~418°C, the reaction products was primarily paraffins with a conversion of 20~65%.¹²⁾ They also concluded that the zeolite component was active in

olefin hydrogenation.

However, the detailed mechanism of the hydrogenation over the zeolite could not be clarified from the present work because of the limited data. A further study is now being carried out and the results will be reported in another paper.

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要 旨

H-ZSM-5 ゼオライト上でのオレフィンの水素化

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H-ZSM-5 ゼオライトのオレフィン水素化能を調べるため、1段目の反応管に Zn-Cr 系メタノール合成触媒、2段目の反応管に H-ZSM-5 ゼオライトを充てんした2段反応装置を用いて、メタノールを経由する合成ガスからの炭化水素合成を検討した。1段目の反応圧を 40 kg/cm² とし、2段目の反応圧を 5~45 kg/cm² と変化させたときの結果を Fig. 1 に示す。2段目の反応圧が 20 kg/cm² 以上では、エタン、プロパンは生成したが、エチレン、プロピレンは全く生成しなかった。このことは、これらパラフィンが H-ZSM-5 ゼオライト上で水素化あるいは水素移行反応により生成したことを示唆している。この違いを明らかにするため C₂H₄-H₂, C₂H₄-He の2種類の混合ガスを H-ZSM-5 ゼオライトに導入した (Fig. 2)。C₂H₄-H₂ 系では、エタン収率は反応温度と共に著しく増大し、545°C では導入したエチレンの 95% がエタンとして検出され

た。一方、水素移行反応によるパラフィン生成の可能性を調べるため行った C₂H₄-He 系では、550°C で導入したエチレンの 10% がエタンとして検出された。したがって、C₂H₄-H₂ 系で生成したエタンの大部分はエチレンの水素化により生成したことになる。

また、Fig. 3 には、不純物の影響を調べるため、Fe を導入した ZSM-5 型ゼオライトを用いて合成ガスの転化反応を行った結果を示す。Fe(II) より調製した ZSM-5 型ゼオライトの生成物はオレフィン指向であった。Fe(II) と Al より調製し、プロトン化した酸点をもつ H-ZSM-5 型ゼオライトの生成物はパラフィン指向であった。

以上の結果より、H-ZSM-5 ゼオライトはオレフィン水素化能を有していると結論した。

Keywords

Hydrogenation, Olefin, Synthesis gas, Zeolite ZSM 5