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Propane Conversion to Aromatic Hydrocarbons on Pt/H-ZSM-5 Catalysts

It is feared that the supply of petroleum resources will become limited in the near future. Therefore, more effective utilization of the huge amounts of light paraffinic hydrocarbons which are contained in natural gas and are produced in petroleum refining processes has become important. Recently, it has been reported in some patent literatures from Mobil Oil and British Petroleum that ethane can be converted to aromatic hydrocarbons using ion-exchanged H-ZSM-5, i.e., Cu–Zn/H-ZSM-5 (*1*), Ga/H-ZSM-5 (*2*), and Ga-exchanged aluminosilicate (*3*). However, since the ethane conversion and the selectivity for aromatics were not high, more extensive studies on catalyst and reaction characteristics should be necessary. The purpose of this study was to develop a novel catalyst for the selective conversion of propane to liquid fuel or aromatic compounds. The catalyst was prepared by the combination of a dehydrogenation catalyst (Pt) and a shape-selective zeolite (H-ZSM-5).

An H-ZSM-5 having a Si/Al atomic ratio of 40 was prepared by a modified method (*4*). Platinum was supported by incipient impregnation or by ion exchange. Platinum tetrammin dichloride was used as a Pt source. After molding the Pt-loaded H-ZSM-5 into tablets, the catalyst was crushed to 10–20 mesh for use in the reaction.

An ordinary flow reaction apparatus was used under atmospheric pressure. A 0.5-g portion of the catalyst was placed in a fused-silica tube reactor of 6 mm inner diameter. The reaction gas, composed of 20% C_3H_8 and 80% N_2, was introduced into the reactor with a space velocity of 2000 hr^{-1}. The temperature was raised at the rate of 0.8°C min^{-1}. The effluent gas composition was analyzed by a gas chromatograph equipped with an integrator. Columns of MS-5A, Silicon OV, and VZ-10 were used.

Activities of various Pt/H-ZSM-5 catalysts are shown in Fig. 1 as well as the activity of H-ZSM-5. Although the propane conversion on H-ZSM-5 catalyst was very low, that on Pt/H-ZSM-5 catalysts began to increase at about 300°C, and attained high conversion levels above 450°C. The propane conversion for 0.5 wt% Pt/H-ZSM-5 prepared by ion exchange was 90% at 500°C, which was higher than that of the impregnated catalyst, i.e., 70%. The higher activity of the ion-exchanged catalyst can be attributed to the higher dispersion of platinum metal particles. As can be seen in Fig. 1 the activity increased with increasing Pt loading.

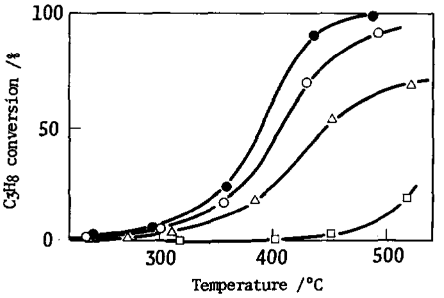

FIG. 1. Temperature dependence of propane conversion for three kinds of Pt/H-ZSM-5 catalysts and H-ZSM-5. Feed gas: C_3H_8 20%, N_2 80%, $SV = 2000$ hr^{-1}; ●, 1.0 wt% Pt/H-ZSM-5 (ion exchange); ○, 0.5 wt% Pt/H-ZSM-5 (ion exchange); △, 0.5 wt% Pt/H-ZSM-5 (impregnation); □, H-ZSM-5.

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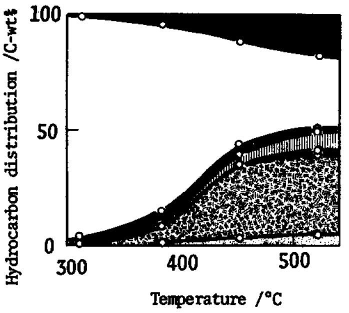

FIG. 2. Hydrocarbon distribution of effluent gas in the case of 0.5 wt% Pt/H-ZSM-5 (impregnation). Feed gas: C_3H_8 20%, N_2 80%, SV = 2000 hr^{-1}; ■, Aromatics; ■, C_{4+} Aliphatics; ▥, C_3H_6; ■, C_2H_4; ▨, C_2H_6; ░, CH_4; □, C_3H_8.

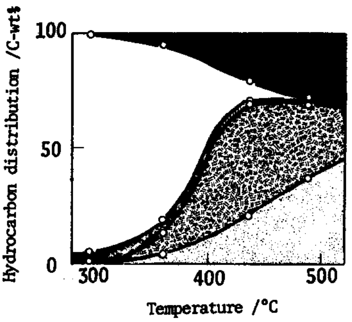

FIG. 4. Hydrocarbon distribution of effluent gas in the case of 1.0 wt% Pt/H-ZSM-5 (ion exchange). Feed gas: C_3H_8 20%, N_2 80%, SV = 2000 hr^{-1}; ■, Aromatics; ■, C_{4+} Aliphatics; ▥, C_3H_6; ■, C_2H_4; ▨, C_2H_6; ░, CH_4; □, C_3H_8.

The temperature dependence of the hydrocarbon distribution of the effluent gas for each catalyst is shown in Figs. 2, 3, and 4. It is noteworthy that a major part of products heavier than C_3 hydrocarbons were aromatics at temperatures higher than 400°C, and that most of the lower carbon-number hydrocarbons, less than C_3, were ethane and methane. In every case, aromatic hydrocarbons increased with increasing temperature. Major parts of the aromatic hydrocarbons were toluene, benzene, and xylene. On the other hand the selectivity for aromatic hydrocarbons on the H-ZSM-5 catalyst was very low and the C_2–C_3 olefin selectivity was high. This indicates that dehydrogenation on Pt is an important step in this reaction process.

The mechanism of this reaction is considered to be as follows: propane is first dehydrogenated into propene by the catalytic action of Pt, and then propene molecules are oligomerized into heavier olefins, followed by the formation of aromatics on the acidic sites of H-ZSM-5 (*5*). However, the heavier olefins formed were decomposed into ethane and methane on the Pt catalyst owing to the high temperature, but the aromatics were stable even at these temperatures. Consequently, most of products were limited to ethane, methane, and aromatics. The retardation of C_1–C_2 hydrocarbon formation is still necessary.

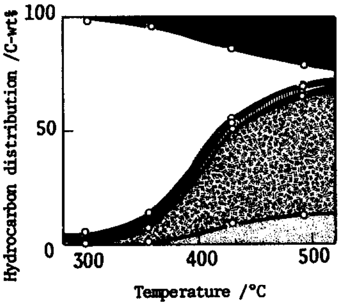

FIG. 3. Hydrocarbon distribution of effluent gas in the case of 0.5 wt% Pt/H-ZSM-5 (ion exchange). Feed gas: C_3H_8 20%, N_2 80%, SV = 2000 hr^{-1}; ■, Aromatics; ■, C_{4+} Aliphatics; ▥, C_3H_6; ■, C_2H_4; ▨, C_2H_6; ░, CH_4; □, C_3H_8.

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