IR observation in methylcyclohexane dehydrogenation over Pt/TiO₂ and Pt/Al₂O₃ catalysts

Kei Watanabe, Yuya Bandai, Ryo Watanabe, Yosiumi Kohno and Choji Fukuhara* Department of Applied Chemistry and Biochemical Engineering, Shizuoka University, Hamamatsu, Shizuoka, Japan *E-mail: tcfukuh@ipc.shizuoka.ac.jp

Organic chemical hydrides are promising candidate materials for hydrogen storage and transport. One of the most promising cycle is methylcyclohexane (MCH) dehydrogenation and toluene (TL) hydrogenation (eq.1).

 $C_7H_{14} \rightleftharpoons C_7H_8 + 3H_2, H^{0}_{298K} = 205 \text{ kJ} \cdot \text{mol}^{-1}(1)$

In order to construct an efficient MCH-TL cycle process, it is required to develop a highly active and stable catalyst for MCH dehydrogenation [1]. Pt/TiO_2 is one of the high performance catalysts. The object of this study is to investigate the catalytic performance and TL adsorption state over Pt/TiO_2 catalyst in comparison with Pt/Al_2O_3 catalyst [1].

Pt/TiO₂ and Pt/Al₂O₃ catalysts were prepared by ion-adsorption method using H2PtCl6·6H2O as platinum precursor. The catalysts were calcined at 500°C for 5 h. The MCH dehydrogenation performance was investigated using a fixed bed reactor. Before reaction, the catalyst was reduced by hydrogen at 350°C for 30 min. The dehydrogenation was then carried out at 350°C with LHSV 35 h⁻¹. The effluent gas was then analyzed using GC-TCD. The conversion was calculated on the basis of MCH consumption. Meanwhile, the adsorption state of TL was observed by FT-IR. TL is adsorbed at 50°C for 30 min under partial pressure of 1.0×10^{-3} atm. Prior to the introducing TL, the catalyst was oxidized at 500°C for 30 min, and followed by a reduction at 350°C. Temperature programed desorption (TPD) measurement was then performed.

Fig.1 shows MCH conversion over Pt/TiO_2 and Pt/Al_2O_3 catalysts with time on stream. The TL selectivity of both catalysts was 100% during the reaction. The Pt/TiO_2 catalyst shows higher activity and better stability than Pt/Al_2O_3 catalyst. The amount of deposited carbon on Pt/TiO_2 and Pt/Al_2O_3 catalysts were 0.4 and 2.9 wt%, respectively. In terms of deactivation, Pt/TiO_2 catalyst showed a high tolerance to coke deposition, which might contribute to a high stability of catalyst.

Figs. 2(a) and 2(b) show TL-TPD spectra of Pt/Al_2O_3 catalysts. Pt/TiO₂ and These experiments were performed from 50°C to 350°C. In Fig. 2(a), v(C=C) stretching band (1600, 1500 cm⁻¹) and v(C=O) stretching band (1690 cm⁻¹), were observed at 50°C on Pt/TiO₂ catalyst [2]. The v(C=C) band decreased with an increase in temperature. The v(C=C) band completely disappeared at 150°C due to a desorption of TL from the catalyst surface. As for Pt/Al_2O_3 catalyst, the v(C=C) band was also observed at 50°C. Although the band at v(C=C)slightly decreased at 100°C, it was remained at high temperature of 350°C. This result indicated that TL was strongly adsorbed on Pt/Al₂O₃ than Pt/TiO₂. In general, strong TL adsorption causes coke deposition [1]. Therefore, Pt/TiO₂ catalyst shows the better coke resistance than Pt/Al₂O₃ catalyst.



Fig. 1 MCH conversion over Pt/TiO₂ and Pt/Al₂O₃ catalysts.



Fig. 2 IR spectra of TL-TPD over (a) Pt/TiO_2 and (b) Pt/Al_2O_3 catalysts.

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