

Catalytically Active Species for Methylation of Benzene with Methane on Co/ZSM-5 Zeolite

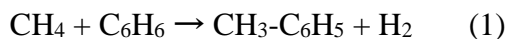
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Methane has not been widely used as a chemical resource due to chemical inactivity. Oxidation of methane into methanol has extensively been studied, but the difficulty is being clarified. We studied methylation of benzene with methane (1) and found Co/ZSM-5 zeolite with higher catalytic activity than previously reported catalysts [1], e.g., In/ZSM-5 [2]. The found reaction rate has been still low, but investigation for functions of catalytic components should open a way to improve the activity. In this study, the ion-exchange behavior and physicochemical properties of surface species were investigated.



Co/ZSM-5 was prepared by impregnation or ion exchange on NH₄-ZSM-5 (Si/Al = 12). The catalytic activity was evaluated by a fixed bed flow method. After the pretreatment in N₂ at 550 °C, methane and benzene were fed at 500 °C, 101 kPa (P_{CH_4} and $P_{\text{C}_6\text{H}_6}$ = 98.6 and 2.7 kPa, respectively) and $W / F = 3.97 \text{ g h mol}_{\text{total gas}}^{-1}$. The acidic property was measured by ammonia infrared mass spectroscopy / temperature-programmed desorption (IRMS-TPD) [3]. X-ray absorption spectrum (XAS) was measured in BL01B1 of SPring-8.

Fig. 1 shows the activity and the numbers of Brønsted (B) and Lewis (L) acid sites on Co-impregnated or ion-exchanged ZSM-5. The activity was negligible on the parent zeolite (Co/Al = 0%). It was generated by Co loading, significantly increased in 30-60% of Co/Al ratio and showed the maximum at 60%. Behavior of change in the activity was similar to that of the number of L acid sites, whereas the B acid sites monotonously decreased with Co loading and were not related with the

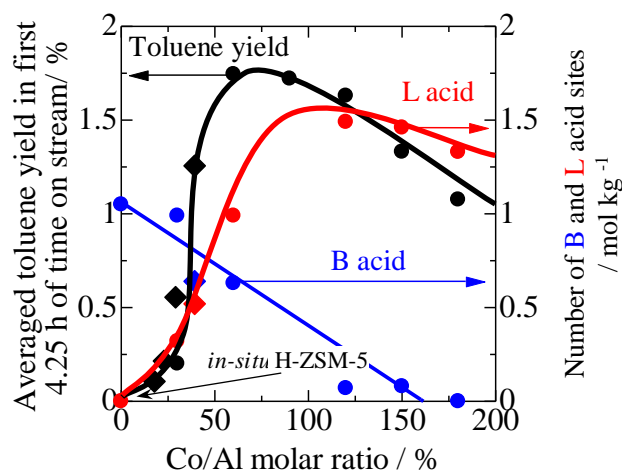


Fig. 1 Catalytic activity for methylation of benzene with methane and numbers of Brønsted and Lewis acid sites on Co-impregnated (●) and ion-exchanged (◆) ZSM-5 zeolite with Si/Al = 12.

activity. This simply shows that the ion exchange of NH₄ by Co proceeded even by the impregnation method where the zeolite was put into a Co nitrate solution and heated to dry up. We can point out that the ion exchange (not impregnation) using excess of Co resulted in the 40% Co/Al ratio. XAS showed that the valence of Co was close to 2 on Co/ZSM-5 shown here after the pretreatment in the same conditions adopted for the reaction. Co was mono-atomically dispersed in the region of Co/Al ratio up to 60% whereas, on Co/ZSM-5-180%, a fraction of Co species were oligomerized or condensed. These indicate that, in addition of bulky Co species at a high loading, at least two kinds of isolated divalent Co species were formed on the MFI zeolite; [A] not working as Lewis acid for ammonia adsorption formed at relatively low loading and [B] adsorbing ammonia as Lewis acid formed at around 60-120% of the Co/Al ratio. The latter should be the active species.

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