# Effect of Second Metal Additive on Co/ZSM-5 Catalyst for Methylation of Benzene with Methane

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Supply of natural gas and shale gas has increasing, and their main component, methane, has attracted much attention as chemical resource alternative to petroleum. However, the activation of methane is very difficult due to the high chemical stability. In our previous study, we found that the Co/ZSM-5 zeolite showed high catalytic activity for methylation of benzene with methane ($CH_4 + C_6H_6 \rightarrow C_6H_5\text{-}CH_3 + H_2$) [1]. On the other hand, it has been well known that the Co/zeolites showed catalytic activity for selective reduction of $NO_x$ with methane and the activity was improved by additive of second metals such as Pt [2]. On these backgrounds, in this study, we attempted the addition of second metal elements to the Co/ZSM-5 catalyst for methylation of benzene with methane.

Cobalt and second metal loaded ZSM-5 catalysts (Co-Me/ZSM-5) were prepared by ion exchange on $NH_4$-ZSM-5 zeolite (Si/Al = 12) with a mixed solution of cobalt nitrate (Co/Al = 200%) and second metal nitrate or chloride (Me/Al = 200%) at 70 °C for 4 h followed by filtration and drying. The amount of cobalt and second metal containing in the final catalysts were investigated by inductively coupled plasma - atomic emission spectrometry (ICP-AES). The catalytic activity was evaluated by a fixed bed flow method. After the pretreatment in $N_2$ at 550 °C, methane and benzene were fed at 500 °C, 101 kPa ($P_{CH4}$ and $P_{C6H6}$ = 98.6 and 2.7 kPa, respectively) and $W / F$ = 3.97 g h $mol_{totalgas}^{-1}$.

The ICP-AES analysis showed that the ratios of total ion-exchanged metals (Co+Me) to Al were approximately constant about 45-50%. Most of the employed second elements were divalent as well as cobalt, and therefore most of the ion-exchange sites in ZSM-5 are considered to be covered by cobalt and metal ions. The amount of cobalt contained in the catalyst was dependent on the period of added elements, as the earlier period, the lower Co/Al ratio. Thus, 3rd and 4th period elements such as Mg, Ca, and Zn tended to substitute prior to cobalt.

Fig. 1 shows the activity for direct methylation of benzene with methane plotted against Co loading. In the case of Co/ZSM-5, the catalytic activity was strongly dependent on the amount of Co. The toluene yield drastically increased at >25% of the Co/Al ratio. On the other hand, Co-Me/ZSM-5 showed the activity strongly dependent on the second additives, resulting in the different activity from that estimated from the activity on Co/ZSM-5 with the equivalent Co content. The catalytic activity higher than that on Co/ZSM-5 with equivalent Co content was found with typical elements such as Mg, Zn, Pb, and Ca but not with transition metals.

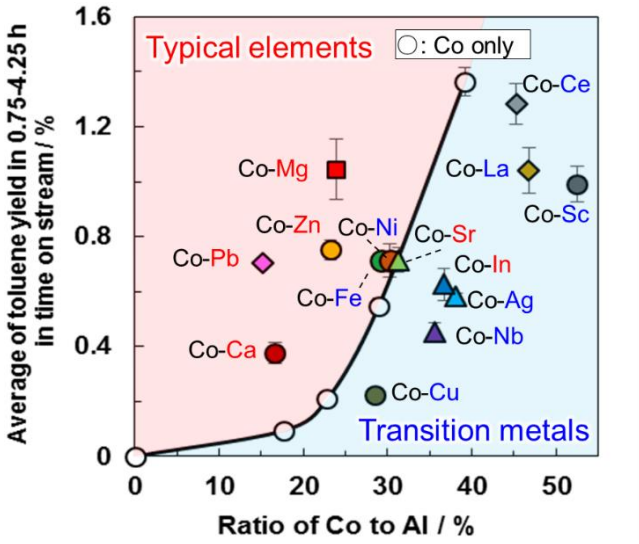


Fig. 1 Relationship between activity for methylation of benzene with methane and amount of cobalt containing in Co/ZSM-5 IE (Co/Al in exchange solution = 20-200%) and Co-Me/ZSM-5 IE-200%-200%, prepared under 200% of Co/Al and 200% of metal/Al ratio in exchange solution, with ■: 3rd, ●: 4th, ▲: 5th and ◆: 6th period elements.

## REFERENCES

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[2] L. Gutierrez, A. Boix, J.O. Petunchi, J. Catal., 179 (1998) 179-191.