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学 位 論 文 の 概 要 及 び 要 旨

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題　　目 Analysis and Design of Active Cobalt Species on MFI Zeolite for Catalytic Methylation of Benzene with Methane
（メタンによるベンゼンのメチル化反応に活性なMFIゼオライト上のCo種の解析と設計）

学位論文の概要及び要旨

In this study, active Co species on MFI zeolite for catalytic methylation of benzene with methane ($CH_4 + C_6H_6 \rightarrow H_3C\text{-}C_6H_5 + H_2$) were analyzed and designed. The influences of second element additive on the catalytic activity of Co/MFI for the reaction were studied to find a method of improving the catalytic activity. The reaction mechanism on Co/MFI catalyst was investigated by in situ FT-IR spectroscopy. The crystallographic position and acidic properties of the Co species in MFI were analyzed with UV-vis spectroscopy and an ammonia IRMS-TPD method to identify the active and inactive Co species for the reaction. Furthermore, the Al concentrations in Co/MFI for selective methylation of benzene were studied. These studies are new guidelines for the design of catalysts for methane conversion reactions.

This thesis is summary of those analyses and experiments composed with six chapters.

Chapter 1 is general introduction. Background and purpose of this study are mentioned.

In the Chapter 2, selective formation of active cobalt species for direct methylation of benzene with methane on MFI zeolite by co-presence of secondary elements is described. The catalytic activity for the methylation of benzene with methane was found on Co/MFI zeolite; the activity was generated by loading of Co in the region of Co / Al molar ratio in the final solid = 0.2 - 0.6 (significantly increased at 0.25 - 0.4) on a support MFI with [Al] = 1.3 mol kg^{-1}. Even in the low Co / Al region, addition of typical divalent elements such as Mg, Zn, Pb and Ca during the Co loading process was found to generate the catalytic

activity. It is speculated that the active cobalt species were selectively formed by the addition of the typical divalent elements.

In the Chapter 3, investigation of reaction mechanism on Co/MFI catalyst for methylation of benzene with methane by using in situ Fourier transform infrared (FT-IR) spectroscopy is described. It was found that C_6H_6 was adsorbed on the Co species in MFI by the introduction of C_6H_6 into Co/MFI. The electronic state of C_6H_6 adsorbed on Co species differed compared with that of free C_6H_6 in the gas phase. In the experiments in which C_6H_6 was flowed, followed by flowing of CH_4 or N_2, the desorption rate of C_6H_6 adsorbed on Co species was faster with CH_4 than with N_2. This indicates that the C_6H_6 previously adsorbed on the Co species in MFI reacted with CH_4, and the methylation of C_6H_6 proceeded.

In the Chapter 4, position and Lewis acidic property of active Co species on MFI zeolite for catalytic methylation of benzene with methane are described. Crystallographic position and acidic properties of the Co species in MFI ([Al] = 1.3 mol kg^{-1}) were investigated with ultraviolet-visible absorption (UV-vis) spectroscopy and an ammonia infrared-mass spectroscopy temperature-programmed desorption (IRMS-TPD) method. The loading of Co^{2+} at the α site in MFI proceeded mainly in the relatively high Co concentration region (Co / Al > 0.25) without additive or in the low Co concentration region in the co-presence of Mg and Pb. On the other hand, the Co species of L1S Lewis acidic type possessing strong base-stabilizing and electron-withdrawing nature showed similar dependency on the Co content to the Co^{2+} at the α site as well as the catalytic activity for the methylation of benzene with methane. These observations indicate that the Co^{2+} at the α site with L1S nature was active for the direct methylation of benzene with methane.

In the Chapter 5, effect of Al concentrations in Co/MFI catalysts for selective methylation of benzene with methane is described. The $[Al]_{Framework}$ in Co/MFI affected the catalytic performance for the methylation of benzene with methane. The Co species loaded on MFI with high $[Al]_{Framework}$ ($[Al]_{Framework}$ > 0.7 mol kg^{-1}) tended to be deactivated by the side reaction (simple dehydrogenation of methane). The Co species impregnated on MFI with $[Al]_{Framework}$ of about 0.3 mol kg^{-1} showed high toluene yield and methylation selectivity. Furthermore, the decreasing in [Co] on the MFI with $[Al]_{Framework}$ = c. a. 0.3 mol kg^{-1} tended to increase the methylation selectivity.

Chapter 6 shows conclusions. It totally summaries this study with main results and knowledges.