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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 Zeolite-based Catalysis
for Production of Benzene Derivatives

(ベンゼン誘導体製造のためのゼオライトに立脚する触媒作用の解析と設計)

学位論文の概要及び要旨

In this study, two fields related to catalysis were mainly studied for improving production process of useful benzene derivatives. The one was related to reaction mechanism of benzene derivatives over solid acid catalysts. Reaction rates of dealkylation and trans-alkylation of alkylbenzenes over various catalysts were analyzed to find the structure of transition state, based on relationship between the activation enthalpy and entropy. It clarified the points of catalyst to be improved. The other was development of benzene methylation with methane. Toluene was found to be produced in methane and benzene flow over Co/MFI zeolite. It was evidenced that the toluene definitely came from reaction of the methane and benzene. The active species on the Co/MFI and reaction behavior of methane and benzene were analyzed by using temperature programmed reaction technique to unveil the way for designing of highly active catalyst. Furthermore, this knowledge was applied to a reaction of ethane and benzene to produce ethylbenzene. These studies led novel process for efficient utilization of unused hydrocarbon resources into conventional chemical industry.

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

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

In the Chapter 2, kinetic analysis of reactions related benzene derivatives over solid acid catalysts is described. The author performed toluene disproportionation and cumene cracking over various acid solid catalysts in various temperature. The catalytic activity was normalized by number of acid sites measured with ammonia infrared mass spectrometer / temperature programmed desorption (NH₃-IRMS-TPD). Results of the reactions were kinetically analyzed with Eyring equation to calculate the activation enthalpy ($\Delta H^{*\circ}$) and entropy ($\Delta S^{*\circ}$). Compensation effects between $\Delta H^{*\circ}$ and entropy $\Delta S^{*\circ}$ were observed in both the reactions and compared with results of light alkane cracking previously reported by our group. The slopes were in order of [cumene cracking] > [toluene disproportionation] > [C₃₋₈ alkane cracking]. The

author applied theory of host-guest chemistry to our heterogeneous catalytic system and considered that the difference of slopes was depended on the bulkiness of reactant molecule as cumene > toluene > small alkane.

In the Chapter 3, direct methylation of benzene with methane over Co/MFI catalyst is described. Various elements supported on zeolites were evaluated for direct methylation of benzene with methane, and cobalt supported on MFI-type zeolite (Co/MFI) catalyst was found to be distinctly active for the reaction. Co/MFI with SiO₂/Al₂O₃ molar ratio = 22 and Co/Al molar ratio = 0.6 showed the highest activity. ¹³C isotope experiments demonstrated that the methyl group and benzene ring of the toluene were origin from methane and benzene, respectively. Quantitating the reaction products with MS clarified that stoichiometry of the target reaction was correct and dehydrogenation of methane was promoted as a side reaction. Co/MFI was characterized with advanced spectroscopic techniques such as NH₃-IRMS-TPD and X-ray absorption spectroscopy to identify the active species. It was clarified that Lewis acidic cobalt (+II) cation monoatomically dispersed on ion exchange site of MFI zeolite was the active species for the reaction.

In the Chapter 4, reactivity of methane and benzene over metal/MFI zeolite analyzed with temperature-programmed reaction technique is described. Methane and benzene were flowed over various elements supported on MFI in 373-843 K, and ion currents originated from the reaction products were recorded with MS. Based on change of the ion currents, oxidation state of the metal species was speculated to be oxidized or reduced during the reaction, and it was clarified by X-ray absorption near edge structure spectra about Co, Pd and Pt/MFI. Oxidation state of cobalt (+II) on ion exchange site was stable even reductive methane + benzene flow at 843 K, whereas some metals represented with noble metals such as Rh, Pd and Pt were reduced into metal(0) species. Toluene and dihydrogen formation rate and methylation selectivity were calculated from the ion currents. Ni, Co, and noble metals such as Rh, Pd and Pt showed high toluene formation rate in the metal/MFI catalysts. However, Ni and noble metals were also highly active for the dehydrogenation, resulting in low methylation selectivity and quick deactivation. On the other hand, cobalt (+II) was stable as oxidized state during the reaction, and therefore it showed stable catalytic activity.

In the Chapter 5, enhancement of methylation selectivity in benzene methylation with methane over Co/MFI is described. Based on knowledges for the active species for the reaction and techniques, methane + benzene TPR was performed over various Co/MFI with different Co and Al content ([Co] and [Al]). Co/MFI with low [Al] showed high methylation selectivity at high temperature realizing that toluene formation rate was over 2.0 μmol g⁻¹ min⁻¹, and long catalytic life over 30 h in continuous flow reaction at 813 K.

In the Chapter 6, production of benzene derivatives from ethane + benzene over Pb/MFI catalyst is described. Reactivity ethane and benzene over various metal supported on MFI-type zeolites were evaluated. Zn, Mo, Pt, and Pb/MFI showed high activity for production of ethylbenzene, styrene, diethylbenzene. Among them, on Zn, Mo, Pt, formation rates of naphthalene, toluene, and C_{3,5} hydrocarbon as byproducts were also high, leading catalyst deactivation. On the other hand, on Pb/MFI, formation rates of the byproducts were slow, realizing high catalytic stability.

Chapter 7 shows conclusions. It totally summaries this study with main results and knowledges.