論文 / 著書情報
Article / Book Information

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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 系 応用化学 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 工学 ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

This dissertation focuses on the catalytic dehydrogenative coupling of alkanes and benzenes as a novel procedure for alkane conversion and C-C bond formation reaction. In order to achieve this target, a search for a catalyst that can selectively reacts with only solid acid for the alkylation was initially conducted. There are no reports of heterogeneous noble-metal-free catalysts for selective alkylation of benzene with simple alkanes. In Chapter II, I focused on montmorillonite (mont), which has been reported as a highly active solid acid in low-temperature liquid-phase organic synthetic reactions. It is known that mont can freely exchange cations in its interlayer and can control its interlayer distance depending on the water content and other factors. In this study, we investigated a catalyst that can obtain the target product with high selectivity by the controlled interlayer distance with exchangeable cations and various treatments. The reaction of *n*-heptane with benzene using various solid acid catalysts was performed at 150 °C. Al-exchanged montmorillonite (Al-mont) gave the desired alkylbenzene of carbon chain 7 in the highest yield. The reaction mechanism in each solid acid was discussed, focusing on the difference in the selectivity of the product depending on the solid acid. In particular, in the case of proton-exchanged montmorillonite (H-mont), the selectivity of the products changed significantly depending on the pretreatment, such as thermal heating and sonication during the preparation, which was concluded to be due to the change in the interlayer distance.

In Chapter II, I have described on the dehydrogenative coupling reaction of alkanes with benzene using only solid acid. However, the yield was low, and the results indicate the rate-limiting step is atomic hydrogen desorption from catalyst surface. Previous reports on stabilization of hydrogen atoms in zeolites suggest that hydrogen desorption is unfavorable from solid acids. In other words, it is mandatory to promote hydrogen desorption to achieve higher efficiency in this reaction. It has reported that mixing a supported metal physically enhances hydrogen desorption through the interparticle hydrogen transfer. Therefore, in Chapter III, I attempted to apply a catalyst mixture of solid acid and supported metal to a catalytic reaction in which hydrogen desorption promoted via interparticle hydrogen transfer. As the supported metal, Pd supported on hydrotalcite, which is highly active in the dehydrogenation reaction to produce hydrogen, was used. The reaction mechanism was assumed to include interparticle hydrogen transfer: hydrogen atoms extracted by solid acid move to the Pd particles to recombine and release as molecular hydrogen.

The reaction promotion mechanism of this catalyst mixture was investigated by structural analysis of the catalysts before and after the reaction, including XAFS, XRD, SEM, and TEM measurements, as well as by reaction experiments under conditions in which the catalysts were not in contact with each other and deuterium labeling experiments. The rate-limiting step of the reaction was also investigated by expanding the substrates to various alkanes and by examining the substrate concentration and catalyst amount.

In Chapter III, I reported on the dehydrogenative coupling reaction between alkanes and benzenes

accelerated by two interparticle hydrogen transfers between Al-mont and Pd/HT. In Chapter IV, I investigated the supported metal species, which is active in hydrogen recombination, to improve the functionality of Pd/HT. After screening various metal-supported catalysts, the highest yield of the target product was obtained using Pt/HT. In the reaction of *n*-heptane with benzene, the target alkylbenzene yield of 24% was achieved at 150 °C in 16 h. I also searched for the best solid acid, and an extremely high selectivity of 99% for the target product was achieved when H-mordenite was used. It was found that the product selectivity strongly depends on the type of solid acid, especially zeolite, suggesting the selective synthesis of alkylation product by the molecular sieving effect of zeolite. The optimal zeolite structure was depended on the size of alkane: the highest product selectivity was observed, in particular, with H-mordenite for *n*-heptane and H-ZSM-5 for cyclopentane, respectively.

The dehydrogenative coupling of simple alkanes and benzene was achieved by the physical mixing of solid acid and supported metal. The slurry-phase interparticle hydrogen transfer between the solid acid and supported metal was the crucial factor in accelerating dehydrogenative coupling. Considering the potential combinations of various solid catalysts, this discovery introduces a novel strategy for developing a combined catalytic system for liquid-phase organic synthesis, including inert bond activation.