

Investigation of Soft Lewis Acid Function in Supported Noble Metal Nano-catalysts for Sustainable Synthesis

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論 文 内 容 の 要 旨

Metal oxide supported noble metal catalysts show many significant advantages such as low cost, high durability, and mass-producibility. In research on supported catalysts, investigating and determining the real active species and sites on the inorganic solids in various reactions were important. However, the supported noble metals are distributed rather than single species, and the reaction mechanism has not been well elucidated compared to molecular catalysts. Therefore, their research was inadequate, which hindered their industrialization. In this research, study on the development and analysis of soft Lewis acid functions of metal oxide supported noble metal catalysts was performed, and the application of these reusable soft Lewis acid catalysts can offer new opportunities for industrial processes and syntheses.

In the hard-soft acid-base (HSAB) principle, Lewis acids can be classified into hard and soft acids which can activate corresponding hard or soft bases. In industrial catalytic reactions, zeolites, typical hard acids, have been widely used. However, most reactions over soft Lewis acids were still using homogeneous catalysts. The low-valent noble metals have soft characteristics and thus should function as a soft Lewis acid to activate soft bases, such as π electrons of C–C double and triple bonds, which easily undergo nucleophilic attack with various nucleophiles. Because the Au and Pt are soft transition metals according to the HSAB principle, the supported Au and Pt catalysts were mainly discussed in this thesis.

It was demonstrated for the first time that supported Pt catalysts with residual chloride can act as a heterogeneous soft Lewis acid. For the application to isomerization of allylic esters, high turnover numbers were realized under solvent-free conditions. X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) analyses reveal that the highly dispersed Pt clusters with Pt–Cl bonds play a key role in the high activity. In addition, DFT calculation and controlling tests verify the reaction mechanism and the enhancement effect in Lewis acidity owing to the residual chloride.

Additionally, reusability of Pt-Cl/CeO₂ was investigated, and the activity was proven to be recovered. XAFS was used to understand the deactivation mechanism of the catalysts. The reduction of PtO_xCl_y species should be the main reason for deactivation. A relatively stable state may occur during the reusing of Pt-Cl/CeO₂.

To develop a more stable soft Lewis catalysts, research on the catalytic isomerization of allylic esters with zirconia supported Au nanoparticles (NPs) succeed. It offers a practical application in the transformation between but-3-ene-1,2-diyl diacetate (3,4-DABE) and but-2-ene-1,4-diyl acetate (1,4-DABE), valuable intermediates of butanediol or THF. Furthermore, a total turnover number (TON) of more than 38,000 are available by flow reaction with the total scale up to kilogram. Meanwhile, there is no obvious deactivation despite slight agglutination of Au NPs.

Moreover, supported sodium-salt-modified Au NPs catalyst was developed, and it was stable and recyclable in the intramolecular cyclization of alkynoic acids. The effect of sodium species, which has been overlooked in previous studies, was studied, and they were found to play an essential role. In addition, the relationship between the kinetics and size of Au NPs revealed that the active sites of the catalyst are located on the surface of Au NPs. Detailed kinetic studies revealed that the cyclization was a zero-order reaction with respect to substrate concentration, and the rate-determining step of the reaction is presumed to be protodeauration.

Furthermore, a practical method for regulating and optimizing the activities of metal-oxide supported Au NP catalysts was discovered. Its effect was investigated in the multiple reactions based on the soft Lewis acid function of Au NPs. By comparing the relationship between specific surface areas and catalytic activities of the prepared metal-oxide supported Au NP catalysts, the catalysts with smaller specific surface area showed better catalytic activity. This trend was obtained in the soft Lewis acid reactions, including isomerization, cyclization, and hydroamination reactions. XPS spectra reveal that the Au NPs supported by the metal-oxides with low specific surface areas tend to have higher binding energy, revealing that more Au^{δ+} species form on their surfaces.

Finally, to further enhance the sustainability of the C4 synthesis process from buta-1,3-diene, one-pot synthesis of THF from 1,4-DABE was also developed by preparing bi-functional Rh/Al-MCM-41 catalysts. In addition, a yield around 60% was obtained using the optimized catalysts.