Abstract

Investigation on Selective Hydrogenation of α-Methylacrolein Over Heterogeneous Catalysts in Gas-Phase

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Selective hydrogenation of α,β-unsaturated aldehydes is widely accepted as a promising chemical process in the synthesis of fine chemicals, such as pharmaceuticals, flavor and perfumes. Considerable efforts have been devoted to develop robust and efficient heterogeneous catalysts to address this long-term issue over the past several decades. In particular, selective saturation of carbonyl group into unsaturated alcohols is comparatively difficult to achieve via conventional and routine catalyst systems from the viewpoint of thermodynamics and kinetics. Although the supported metal catalysts have been currently and extensively documented and been exploited to realize this complicated transformation, the fundamental understanding of reaction mechanism is still at its early stage, and the structure-performance relationship is required to get in-depth insight due to the complexity of heterogeneous catalysts. Nowadays, the concerns about ecology and environment protection, as well as the concept of "green chemistry", are prevalent in the academic field that inspires us to develop more eco-friendly method to realize the selective hydrogenation of α,β-unsaturated aldehydes. In this dissertation, we focus on the gas-phase selective hydrogenation of α-methylacrolein on the purpose of the continuous chemical transformation and abandoning the usage of organic solvent, as well as trying our best to discuss the relevant discovery.

First, the sol-gel method was employed to prepare a series of alumina supported Ni-based bimetallic catalysts for the gas-phase selective hydrogenation of α-methylacrolein. By screening the performances of monometallic Ni catalyst and several M-Ni bimetallic catalysts (M = In, Fe, Cu, Co, Ga and Zn), the outstanding performance for the C=O bond hydrogenation was observed on the In-Ni bimetallic catalysts, which can be explained on account of the synergy between metallic In and Ni, In-oxo species and Al_2O_3 support. As revealed by multiple characterizations, the "structure-matching strategy" is proposed to rationalize the unique geometric and electronic properties of In-Ni bimetallic catalysts. The decoration effect of In component primarily depends on its chemical state. The metallic In species incline to incorporate into metallic Ni lattice in the formation of In-Ni alloy or intermetallic compounds (IMCs), wherein the charge transfer enables the construction of electropositive and electronegative microenvironment ($In^{\delta+}$-$Ni^{\delta-}$) for the preferential adsorption of the C=O bond and delivers the repulsion to the vinyl group on the electron-enriched $Ni^{\delta-}$ sites. On the other hand, the mutual interplay of In-oxo species with Al_2O_3 support contributes to the formation of In-O-Al unites accounting for the heterolytic dissociation of H_2. Therefore, the as-prepared In-Ni catalysts achieves a selectivity of 77.2% to methallyl alcohol at the conversion level of 53.8% under the optimal condition.

Then, the effect of porous architecture of zeolite has been investigated by comparing the performances of original and hierarchical zeolite-supported catalysts. As indicated by the experimental results, the presence of auxiliary mesoporous channels on the hierarchical zeolites offers ample space to accommodate metal nanoparticles, enhancing the accessibility of reactants to active sites and the mass diffusion, which gives the better reactivity. On the other hand, metal Ag showcases distinct performances from the typical transition metals in hydrogenation reactions (such as Ni, Cu, Co and Pt), on which the saturation of C=O bond has a priority to occur. Under the optimal reaction condition, the selectivity to methallyl alcohol reaches ~75% on the hierarchical ZSM-5 and Silicalite-1 zeolite supported Ag catalysts.

Finally, we devote to give an explanation on why metal Ag has such attracting properties on the selective hydrogenation reaction, the "electronic metal-support interaction (EMSI)" is employed as a strategy to tuning the charge state of metal Ag active sites. The experimental results suggested that the product distribution significantly relies on the alteration of electronic structure of metal Ag sites. In the absence of electronic perturbation, Ag^0 sites prefer to adsorb the C=O bond via the π-bonding configuration, while such behavior was overturned on the positively-charged $Ag^{\delta+}$ sites, responsible for the selective hydrogenation of C=C bond. This discovery not only circumvent the selectivity control of chemical reaction, but also enriches the fundamental understanding of bond-oriented recognition, which is necessary for the rational design of Ag-based catalysts in the selective hydrogenation of α,β-unsaturated aldehydes.