A Significant Enhancement of Catalytic Properties by Adjusting Catalyst Wettability

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Abstract: The contribution of catalyst wettability for catalytic performance has been ignored for a long time. In this talk, we have briefly summarized our recent works on the importance of catalyst wettability for improving catalytic activity, product selectivity, and catalyst stability. Suitable catalyst wettability is favorable for several reasons: 1) to enrich the reactants, leading to enhancement of the catalytic activity; 2) to inhibit side-reactions, giving desirable products; 3) to reduce the poisoning of active sites and damage to catalyst framework, resulting in an increase of catalyst stability. These advantages of suitable catalyst wettability will be very important for designing and developing novel heterogeneous catalysts in the future.

Keywords: Catalyst wettability, Catalytic performance, Performance enhancement.

1. Introduction

Normally, heterogeneous catalysis process includes five steps, consisting of reactant adsorption, reactant surface transfer, catalytic conversion, product surface transfer, and product desorption. Clearly, catalytic performance of the heterogeneous catalysts is not only related to the active sites, but also the adsorption and desorption of the reactants and products, as well as their surface transfers.

It is well known that the molecular adsorption and desorption as well as molecular surface transfers are strongly influenced by the catalyst wettability (i.e. the catalyst hydrophobicity and hydrophilicity). The wettability means the compatibility and/or affinity of the heterogeneous catalyst to the liquid reactants in the reaction system. The catalysts with suitable wettability could enhance the adsorption and transfer of reactants or products, leading to enhancement in catalytic performance.

2. Enhancement of catalytic activity by enriched reactants

The enrichment of the reactants in the catalysts is favorable for the shift of reaction equilibrium to products, leading to improvement in catalyst activities. For example, after copolymerization of divinylbenzene and vinyl-functionalized ionic liquid (PDVB-IL), the sample is highly active for transesterification of tripalmitin with methanol. Its activity is even higher than the corresponding homogeneous ionic liquids. This unique character is strongly related to its superhydrophobic nature of the catalyst, which shows excellent wettability to the methanol and tripalmitin reactants according to the reactant droplet contact angle tests, leading to the efficient adsorption and enrichment of organic substrates [1,2].

3. Improvement of catalytic selectivity by inhibiting side-reactions

Catalyst wettability improves not only catalytic activities, but also product selectivities because catalysts with unique wettability can promote or prevent the conversion of products obtained at the first step. A typical reaction for biomass conversion is the catalytic dehydration of fructose into 5-hydroxymethylfurfural (HMF) over acid catalysts, for which there are always by-products of formic acid and levulinic acid, formed by hydration of HMF. Despite considerable progress in suppressing the side-reaction by processes such as phase-modification and water-removal reaction systems, a small amount of formic acid and levulinic acid in the final products remains. Based on theoretical simulation, they found that keeping water molecule away from the acid sites in a non-reaction zone could fully prevent the hydration of HMF. In their experiments they used a superhydrophobic sulfonated PDVB (P-SO$_3$H-154) as an acid catalyst to catalyze the fructose dehydration. Because the acidic sites are isolated from the water molecules,
due to the catalyst superhydrophobicity, the hydration of HMF is completely avoided. As a result, HMF as a sole product has been obtained [3,4].

4. Increase of catalyst stability by reducing damage to catalyst framework

Generally, the deactivation of heterogeneous catalysts originates from poisoning of active sites or damage to the catalyst framework. Overcoming these limitations is a great challenge for the synthesis of efficient heterogeneous catalysts. For example, hydrolytic degradation has caused numerous efficient catalytic systems to suffer because in many cases it is impossible to fully exclude water from the reaction systems. In our case, it is demonstrated an effective strategy of stabilizing water-sensitive organic-ligand-based homogeneous catalysts by constructing them into a superhydrophobic porous framework, which renders them extraordinarily water resistant yet fully retains their intrinsic catalytic activities under heterogeneous systems. Representatively, after metalation of the superhydrophobic porous phosphite-ligand-based framework with Rh species, the resultant catalyst exhibits superior activities and dramatically enhanced durability in mimic continuous hydroformylation processes of the internal olefins in comparison with the homogeneous counterparts. In addition, because it is solid in nature, the catalyst can be readily recycled with negligible loss of performance. Given the modular nature and the broad scope of organic ligands, our work opens a new avenue for stabilizing water-sensitive homogeneous catalysts into highly water-tolerate heterogeneous catalysts [5].

References