A significant enhancement of catalytic performance by adjusting catalyst wettability

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Heterogeneous catalysts have played a crucial role in upgrading fuels, transforming biomass [1–3], removing pollutants [4–6], harvesting solar energy [7–9], and producing fine chemicals [10,11]. Compared with homogeneous catalysts, the heterogeneous catalysts have obvious advantages in easy separation and regeneration from the reaction systems [12–15], but still have unsatisfactory activity and/or selectivity. These issues are reasonably assigned to the limited molecular diffusion on the heterogeneous catalysts. Therefore, it is in great demand to improve the catalytic performances of these catalysts by increasing mass transfer in the reactions, which is always a challenge in the heterogeneous catalysis.

For a general reaction from A and B reactants to C and D products, the rate of a chemical reaction is sensitive to the concentration of the reactants and products, as shown in Equation (1) (r is the reaction rate, $[A-D]$ is the concentration of reactants A–D, $a-d$ is the kinetic reaction order of reactants A–D):

$$r = [A]^a[B]^b / [C]^c[D]^d \quad (1)$$

Therefore, it is reasonable to improve the reaction rate by increasing the concentration of reactants and reducing the concentration of products close to the active centers. Normally, a heterogeneous catalysis [16] mainly includes the adsorption of reactant, reactant transfer on the catalyst surface, reactant conversion from reactants to products, product transfer on the catalyst surface, and desorption of products, as presented in Scheme 1. In these steps, four steps are related to the molecular diffusion in the reaction.

It is well known that the molecular diffusion is strongly influenced by catalyst wettability. The recent results have demonstrated that the adjustment of catalyst wettability would lead to (i) enrichment of the reactants for accelerating the reaction, (ii) fast diffusion of the products for shifting the reaction balance, (iii) formation of new re-

action intermediates, (iv) isolation of undesired molecules for hindering the side reactions, and (v) stabilization of the catalyst structure.

Enrichment of reactants for increasing catalytic activity

As illustrated in Equation (1), enhancement of reactant concentration should effectively increase the reaction rate. In the beginning, it was focused on the zeolite catalysts. One typical example is the industrial TS-1 zeolite with hydrophobic framework, which is not favorable for adsorption of H_2O_2 in the oxidations of organic compounds with H_2O_2 because the H_2O_2 is polar and hydrophilic [17–20]. Obviously, the TS-1 zeolite with more hydrophilicity might be helpful to enrich the H_2O_2 , leading to improvement of the catalytic activities. As expected, Wang *et al.* [21] synthesized hydrophilic TS-1 zeolite by employing organosilicon as precursor, followed by calcination to transform the organic groups into silanol groups. The TS-1 zeolite with more hydrophilic silanol groups exhibits much higher reaction rate ($4.9 \text{ mmol L}^{-1} \text{ min}^{-1}$) than the conventional TS-1 ($0.6 \text{ mmol L}^{-1} \text{ min}^{-1}$) in the oxidation of 1-hexene with H_2O_2 , because the hydrophilic zeolite can effectively enrich the concentration of H_2O_2 reactant in the zeolite micropores, as confirmed by the molecule adsorption and water-droplet contact angle tests. When a chiral modified Pt nanocatalyst was confined within the carbon

Scheme 1 A whole heterogeneous catalysis (R=reactants, P=products).

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Scheme 2 Catalytic strategy for producing bio-furan over a hydrophilic zeolite fixed Pd nanoparticle catalyst. Reprinted with permission from Ref. [33]. Copyright 2018, American Chemical Society.

nanotubes, the activity (turnover frequency (TOF) of $1.0 \times 10^5 \text{ h}^{-1}$) and enantioselectivity (96%) were greatly enhanced in asymmetric hydrogenation of α -ketoesters, compared with the Pt species on the external surface of carbon nanotubes (TOF of $15,000 \text{ h}^{-1}$, enantioselectivity at 75%) [15]. This phenomenon is reasonably assigned to the ultrahigh enrichment of the chiral modifier and reactants within the channels of carbon nanotubes.

Recently, a series of organic porous polymers with controllable wettability have been developed [22–26]. By functionalizing the catalytically active sites into the porous polymers, the heterogeneous catalysts with controllable wettability display excellent catalytic performances. For example, the hydrophobic porous polymer functionalized with acidic ionic liquid groups could efficiently catalyze the transesterification of tripalmitin with methanol to biofuels [27], exhibiting an activity even higher than that of the corresponding homogeneous ionic liquids. This phenomenon is strongly related to the hydrophobic nature of the catalyst with superior wettability to the tripalmitin and methanol reactants, benefiting the adsorption and enrichment of reactant within the nanopores. Furthermore, the chiral ligands [e.g., bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) and *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (TsDPEN)] are also functionalized onto the porous polymer network, followed by coordination with Rh sites to achieve the heterogeneous catalysts. Interestingly, these catalysts give comparable activities and enantioselectivities to those of the corresponding homogeneous catalysts [25,26].

In addition, the strategy for adjusting catalyst wettability is extended to prepare supported metal nanoparticle catalysts and metal-organic frameworks (MOFs)

[28–31]. Cao and co-workers [28] developed hydrophobic carbon supported Pd nanoparticles, showing higher activities for the dehydrogenative coupling of organosilanes with alcohols and amines than those of the existing catalysts. Jiang and co-workers [29] developed a polydimethylsiloxane coating for a Pd/MOF composite, realizing significantly enhanced catalytic performance in nitroarene hydrogenation by enriching the molecules. Huo and co-workers [30] covered Pt loaded MOF crystals with hydrophilic graphene oxide and hydrophobic reduced graphene oxide, achieving different catalysts with selectivity in the hydrogenation of hydrophilic or hydrophobic nitroarene molecules.

Fast desorption of products for increasing catalytic activity and selectivity

Apart from the reactant enrichment, the fast desorption of products to decrease the concentration around the active centers is also favorable for increasing catalytic activity according to Equation (1). In order to adjust the product diffusion, Wang *et al.* [32,33] developed a route for capsulation of catalytically active sites within the zeolite crystals. Because the diffusion rates of various products are quite different in the zeolite micropores, it is possible to achieve high activity and selectivity for the desirable product by adjusting zeolite wettability. For example, furfural hydrogenation has more than eight products on general supported Pd catalysts. However, Pd nanoparticles fixed with the silanol modified silicate-1 zeolite showed a sole furan product at full conversion of furfural (Scheme 2). This phenomenon is reasonably assigned to very high diffusion rate within the zeolite micropores, where the diffusion rate of furan is maximized, while the diffusion of the by-products (furfural, dihy-

drofuran, tetrahydrofuran, and furfuryl alcohol) is strongly hindered. The fast desorption of furan leads to the selective formation of furan as a sole product. Indeed, the controllable molecular diffusion in the heterogeneous catalysis is favorable for the shift of reaction equilibrium to the products, enhancing the catalytic activities and selectivities.

Formation of new intermediates

The adjustment of catalyst wettability not only changes mass transfer of reactants/products, but also promotes the formation of new reaction intermediates. In the hydrogenation of CO_2 into methanol, Peng *et al.* [34] found that the SiC quantum dots exhibit remarkably higher activity ($0.27 \text{ mmol m}^{-2} \text{ h}^{-1}$) than commercial SiC ($0.01 \text{ mmol m}^{-2} \text{ h}^{-1}$). Kinetic studies reveal that the activation energy for SiC quantum dots was 48.6 kJ mol^{-1} , about half of that (94.7 kJ mol^{-1}) for commercial SiC. Further studies show that the SiC quantum dots are hydrophilic due to rich surface hydroxyl groups. These hydroxyls are favorable for the formation of HCOO^* as a new intermediate, which effectively decreases the energy barrier in CO_2 hydrogenation. These results provide unique insights into the role of catalyst wettability for the intermediate formation.

Isolation of water molecules for hindering the side reactions

In the catalytic transformations, the side-reactions usually occur to give by-products. As a typical example, the acid-catalyzed dehydration of fructose has been regarded as a general route for producing 5-hydroxymethylfurfural (HMF), an important biomass-derived platform by US Department of Energy. In this process, the HMF product could be transformed into formic acid and levulinic acid over the acid catalyst by hydration [35]. Considering that the hydration side-reaction occurred between the product and water, it is expected to hinder the side reaction (hydration) by fast removal of the water or HMF away from the acid centers. Wang *et al.* [35] described a strategy to switch off the hydration of HMF by controlling the wettability of solid acid catalysts. By performing the theoretical simulation, it is found that the distance between water and acid sites is sensitive to the hydration. Therefore, separation of water molecules to acidic sites in a non-reaction zone enables switch off the side reaction. On the basis of these findings, a superhydrophobic acid catalyst was developed by co-polymerization of acidic monomers with vinylbenzene, giving a hydrophobic material with water-droplet contact angle at $\sim 104^\circ$. The

Scheme 3 Hydrophobic zeolite for hindering the water diffusion and preventing the side-reaction of hydration.

hydrophobic feature could isolate water molecules from acid centers. In the hydration of fructose, the HMF appeared as a sole product, outperforming the industrial solid acid (Amberlyst-15) and homogeneous acid catalysts (e.g., H_2SO_4) with low HMF selectivity ($<50\%$).

Recently, a persuasive example is oxidative cyanation over manganese oxide-based catalysts for producing organic nitriles [36]. Notably, manganese oxide is a good catalyst for hydration of organic nitriles into amides, giving amides as major products in the oxidative cyanation. The traditional strategy for selective production of nitriles employs the unsustainable post-treatments, such as dehydration with thionyl chloride. Considering that occurrence of this side reaction requires water as a reactant, Wang *et al.* [36] designed the fixation of manganese oxide nanoparticles with hydrophobic pure silica zeolite shells that could remarkably block the hydration of nitriles to amides in the oxidative cyanation, giving high selectivity for nitrile product, as shown in Scheme 3.

Stabilization of heterogeneous catalysts by adjusting the wettability

The stability is an important factor for heterogeneous catalysis. Generally, deactivation of the catalysts results from the damage of catalyst structure and/or poisoning of active sites. The solution to these issues for achieving stable catalysts is still challenging.

The aluminosilicate zeolites have been widely used as industrial catalysts, but they have relatively low stability in hot water (200°C) because of the hydrolysis of Si-O-Si or Si-O-Al bonds to break the zeolite framework. Recently, Zapata *et al.* [37] employed the organic silane to modify the H-USY zeolite via a post-silylation method, obtaining hydrophobic H-USY zeolite. The hydro-

Scheme 4 Hydrophobic zeolite with water resistance at high temperature and conventional zeolite with poor stability in hot water.

phobicity of the catalyst significantly prevents the diffusion of water into the zeolite micropores for destroying the zeolite frameworks. In the catalytic tests of alkylation of *m*-cresol with 2-propanol in biphasic water-oil solvent at 200°C, the hydrophobic H-USY zeolite displays high activity and stability. In contrast, the conventional H-USY zeolite gives unsatisfied activity and stability in the equivalent tests owing to relatively low stability in hot water (Scheme 4).

Compared with zeolites, the MOFs exhibit relatively poor stability even at room temperature in wet air, which is crucial for widely practical applications. Sun *et al.* [38] impart amphiphobicity onto the MOFs by chemically coating the exterior of MOF crystals with F-containing organic groups, giving extraordinary stability. In addition, hydrolytic degradation of water-sensitive organometallic catalysts is a problem in recent years because in many cases it is impossible to fully exclude water from the reaction systems. Sun *et al.* [24] contributed an effective approach for boosting the durability of water-sensitive ligands against hydrolysis *via* the construction of superhydrophobic porous polymers. For example, by introduction of porosity into the phosphite polymers, the phosphite species become water-resistant due to the formation of superhydrophobic phosphite-based catalysts.

The nickel-based catalysts are well-known in the hydrogenations, where a large amount of water in the reactions must be minimized for avoiding the formation of nickel hydroxide. To solve this problem, Lin *et al.* [39] developed an effective method by coating the nickel catalyst with hydrophobic carbon layer. In the hydrogenation of nitroarenes with TiO₂ supported nickel nanoparticles, the catalyst with hydrophobic carbon layer exhibits remarkably enhanced recyclability compared with the catalysts without hydrophobic layer.

In conclusion, we have briefly summarized the preparation of various heterogeneous catalysts with con-

trollable wettability and their catalytic performances. Clearly, the adjustment of catalyst wettability can significantly enhance the catalytic activity, product selectivity, and catalyst stability, which offers a good opportunity for the design and preparation of highly efficient heterogeneous catalysts.

Although dramatic advances have been achieved in the literatures summarized here, there are still many challenges for preparation of heterogeneous catalysts with controllable wettability. For example, it is not easy to adjust the wettability of supported metal nanoparticle catalysts due to the difficulty in controlling hydrophobicity/hydrophilicity of metal nanoparticles. Fixation of the metal nanoparticles within zeolite crystals seems a potential route to overcome this issue, because of the rich porosity and controllable wettability of zeolite crystals. Nevertheless, the methodologies for constructing the heterogeneous catalysts with controllable wettability are still developing.

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通过调控催化材料的浸润性提高其催化性能

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摘要 固相材料的浸润性(包括亲水性、疏水性、亲油性和疏油性)已经成为设计与合成多相催化材料中必须要考虑的因素。总结近年来的实验结果发现, 催化材料的浸润性对分子的扩散有显著影响, 适宜的浸润性与活性中心的协同是增强催化性能的关键, 这可以通过(i)有效富集反应物、(ii)快速扩散产物、(iii)促进形成反应中间体、(iv)避免副反应和(v)提高催化材料结构等因素来提升多相催化材料的活性、选择性和反应寿命, 这为设计与制备高效多相催化材料提供了新机遇。