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Insights into support wettability in tuning catalytic performance in the oxidation of aliphatic alcohols to acids†

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A superhydrophobic catalyst was prepared by immobilizing Pt nanoparticles on superhydrophobic organic–inorganic hybrid silicas, which showed high activity and selectivity in the oxidation of aliphatic alcohols to carboxylic acids.

Supported metal nanoparticle (MNP) catalysts constitute one of the greatly important and the most investigated catalysts in both academia and industry.[1] Substantial studies have focused on developing novel synthetic methods to control metal size, morphology and anchoring methods.[2] Recent discoveries have shown that catalyst supports could modify the electronic state of MNP and consequently influence catalysis.[3] Limited to these studies, the other effects of catalyst supports are greatly overlooked. For example, the wettability (hydrophilicity–hydrophobicity) of supports can directly affect the adsorption and desorption of the reactant and the product, elementary steps in catalysis. Therefore, it is desirable to create a suitable microenvironment on the catalyst surface to facilitate mass transfer.

Catalytic oxidation is a usual way of producing hydrocarbon oxygenates. A critical issue arises in the priority adsorption of the polar products such as water and acids on the hydrophilic sites (–OH, –O(H)–, –O–, defect sites, *etc.*) of supports by virtue of non-covalent bonding interaction.[4] As a result, polar substance layers cover the catalyst surface, limiting reactant diffusion to active sites and usually causing carbon species deposition on active sites. If the surface wettability can be tuned according to the character of reaction, better activity and selectivity can be anticipated. However, the preparation of hydrophobic catalysts with robustness and reusability still remains a challenging task.

We were inspired by recent advances in superhydrophobic materials with the water contact angle (WCA) $\geq 150^\circ$.[5] We thought that superhydrophobic materials can potentially be used as heterogeneous catalysts once suitable catalytic active sites are created on them because of the reasons that (i) their strong water repellent ability can promote desorption of water and acids from the catalyst surface; and (ii) the adhesion to less polar reactants, such as alcohols and aldehydes, can decrease mass transfer resistance on active sites, increasing the activity. Several groups,[6] including ours,[7] have studied post-grafting or co-condensation methods to modify the surface of (Ti, Ta, Co, *etc.*)-doped metal oxide catalysts, and their applications in alkene epoxidation and hydrocarbon oxidation. These preparation methods are experimentally simple, but inherently suffer from inadequate hydrophobicity and/or that the active sites are partially buried or poisoned during preparation. Unlike previous studies, we herein report a novel strategy for constructing metal nanoparticles on the robust superhydrophobic surface of organic–inorganic hybrid silicas. Pt nanoparticles were localized on silica through nitrogen–Pt interaction. The catalyst is highly reactive, selective and recyclable for oxidation of aliphatic alcohols to carboxylic acids. Importantly we show that the surface wettability of supports plays pivotal roles in tuning the catalytic performance.

Phenyl-modified amine-bridged silica (Ph-AOS) was prepared using a water-in-oil reverse microemulsion method (Scheme S1, ESI†).[8] The phenyl groups create a hydrophobic layer on the surface. The amine groups in the framework act as anchoring sites for Pt nanoparticles. Transmission electron microscopy (TEM) images show that the support materials with or without phenyl groups are monodispersed nanospheres with diameter size of ~ 90 nm (Fig. S1 and S2, ESI†).

The material composition was analyzed using Fourier transform infrared (FT-IR), and ^{29}Si magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR) spectroscopy and ^{13}C cross-polarization MAS NMR (^{13}C CP/MAS NMR) spectroscopy (Fig. 1, Fig. S3 and S4, ESI†). In the FT-IR spectra, both samples show C–H vibration bands of the bridging aliphatic carbon chain at 2930, 2883, 1460 and 1414 cm^{-1}, Si–C vibration at 1119 cm^{-1} and the Si–O–Si band at 1032 cm^{-1}.[9] The =CH stretching aromatic vibrations (weak peaks at 3030–3080 cm^{-1}) and mono-substituted benzene out-of-plane bending vibration (739 and 698 cm^{-1}) in the spectrum of Ph-AOS confirm the successful incorporation of phenyl groups.[7c] The ^{29}Si MAS NMR spectrum shows characteristic peaks of the organosiloxane network [$\mathrm{T}^m = \mathrm{RSi(OSi)}_m\mathrm{(OH)}_{3-m}$, m = 1–3] (Fig. 1). The peaks at around -60 and -70 ppm are assigned to [T^3, $\mathrm{CSi(OSi)_3}$] and [T^2, $\mathrm{CSi(OSi)_2(OH)}$] silicon connected with the bridging groups, respectively.[9] The peak

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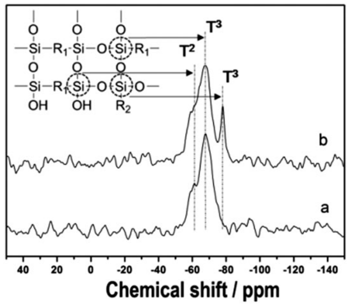


Fig. 1 ^{29}Si MAS-NMR spectra of (a) AOS and (b) Ph-AOS. R_1 and R_2 indicate the bridging group and the phenyl group, respectively.

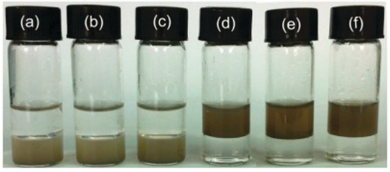


Fig. 2 The dispersion of (a–c) Pt/AOS and (d–f) Pt/Ph-AOS in water (lower phase) and 1-butanol (a and d), butanal (b and e) and toluene (c and f) mixture (upper phase).

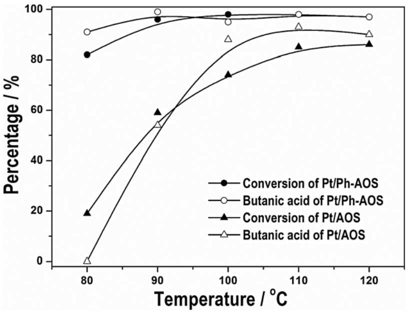


Fig. 3 Catalytic activities of Pt/AOS and Pt/Ph-AOS in the oxidation of 1-butanol. Reaction conditions: 0.2 mmol 1-butanol, 0.05 mmol mesitylene, 10 mg catalyst, 2 mL toluene, 1.0 MPa oxygen, 24 h.

at −78 ppm in the Ph-AOS spectrum is attributed to the [T^3, CSi(OSi)$_3$] silicon connected to phenyl groups. In the ^{13}C CP/MAS NMR spectrum of Ph-AOS, the peaks at 100–150 ppm and below 100 ppm are ascribed to the aromatic carbon in phenyl groups and the aliphatic carbon, respectively (Fig. S4, ESI†). Thermogravimetric analysis (TGA) and temperature programmed oxidation-mass spectroscopy (TPO-MS) indicate that both samples are thermally stable up to 285 °C, after which point the bridging organic groups start to decompose (Fig. S5 and S6, ESI†). Another weight loss at 500 °C in Ph-AOS is caused by the decomposition of phenyl groups.[7b] All these characterizations confirm that the prepared silica has the expected structure. The presence of phenyl groups greatly changed the surface hydrophilicity–hydrophobicity. Water contact angle measurement indicates that the amine-bridged silica without phenyl groups (AOS) is hydrophilic with a WCA of 20° (Fig. S1a, ESI,† the inseted image), and Ph-AOS shows superhydrophobicity with WCA up to 150° (Fig. S1b, ESI,† the inseted image).

We employed the as-synthesized silica as a support for Pt nanoparticles. The Pt nanoparticles with diameter size of 2.48 and 2.51 nm for Pt/AOS and Pt/Ph-AOS, respectively, were supported *via* the N–Pt interaction (Fig. S7 and S8, ESI†). Pt nanoparticles are difficult to be supported on silica without amine groups as anchoring sites (Fig. S9 and S10, ESI†). The Pt content of Pt/AOS and Pt/Ph-AOS was 2.02 wt% and 1.94 wt%, respectively, as analyzed using inductively coupled plasma (ICP). The X-ray photoelectron spectrum (XPS) of Ph-AOS shows N1s (399.3 eV) and C1s (285.0 eV) peaks, indicating that organic groups are present on the material surface (Fig. S11, ESI†). The appearance of Pt4d and Pt4f peaks indicate that Pt particles are localized on the surface. The *in situ* FT-IR spectrum of CO adsorption on Pt/Ph-AOS shows a strong band at 2040 cm^{-1} and a weak band at 1825 cm^{-1}, which are attributed to the linearly bonded CO on Pt atoms and the bridged adsorption of CO on neighbouring Pt atoms, respectively (Fig. S12, ESI†). Compared to the adsorption of CO on metallic neutral Pt (2090–2100 cm^{-1}), a large red shift observed on Pt/Ph-AOS indicates d–π* electron donation from Pt to CO, indicating that Pt is negatively charged.[10] This further proves that nitrogen donates electrons (p–d) to Pt particles. In a 1-butanol (or butanal–toluene) and water mixed solvent, Pt/AOS is dispersed in the lower water phase, and Pt/Ph-AOS is selectively suspended in the upper 1-butanol, butanal and toluene phase (Fig. 2), indicating the hydrophobic nature of Pt/Ph-AOS. Alcohols and aldehydes tend to adsorb onto Pt/Ph-AOS, and water onto Pt/AOS.

We then test their catalytic performance in the selective oxidation of aliphatic alcohols to acids (Fig. 3). The reaction is one of the most important and challenging reactions in organic synthesis.[11] At 80 °C, the reaction over Pt/AOS was sluggish and only 19% conversion of 1-butanol was obtained. The conversion increased with an increase in temperature and reached 80% at 120 °C. For the same reaction over Pt/Ph-AOS, the activity was greatly enhanced. The conversion reached 80% at 80 °C which was nearly four times of that obtained over Pt/AOS. A further increase in temperature to 90 °C completely converted 1-butanol. The main product over Pt/AOS was butanal at 80 °C. Notably the selectivity of butanic acid gradually increased with an increase in temperature. In comparison, the reaction over Pt/Ph-AOS produced butanic acid as the main product, independent of the reaction temperature investigated.

We adjusted the content of phenyl group to obtain silica with differential hydrophobicity, as illustrated by WCA measurement. The WCA increased with an increase in phenyl group contents from 0, 1.3, 1.9, to 2.5 mmol g^{-1} (Fig. S13, ESI†).[12] As expected, the activity and selectivity of the butanic acid increased with an increase in WCA (Fig. 4). This demonstrates that the surface hydrophobicity is favorable for oxidation of 1-butanol to butanic acid.

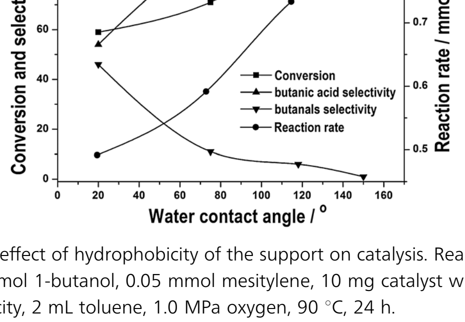
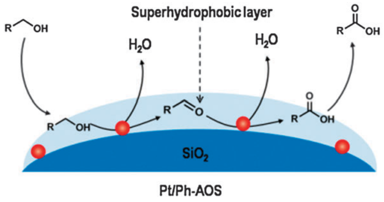


Fig. 4 The effect of hydrophobicity of the support on catalysis. Reaction conditions: 0.2 mmol 1-butanol, 0.05 mmol mesitylene, 10 mg catalyst with different hydrophobicity, 2 mL toluene, 1.0 MPa oxygen, 90 °C, 24 h.



Scheme 1 The process of 1-butanol oxidation over Pt/Ph-AOS.

We attribute the excellent catalytic activity of Pt/Ph-AOS to its surface hydrophobicity (Scheme 1). The surface phenyl groups create a hydrophobic microenvironment and the supported Pt nanoparticles function as active phases. The hydrophobic index (HI) was 3.5 times that of Pt/AOS.[13] This indicates that Pt/Ph-AOS is much more hydrophobic than Pt/AOS. Less polar organic substrates, such as 1-butanol and butanal, can be enriched on the surface of Pt/Ph-AOS, which enable the Pt nanoparticles to have better accessibility to organic molecules, thus resulting in higher conversion. And, the intermediate of butanal can be more easily adsorbed and oxidized over Pt/Ph-AOS than over Pt/AOS to butanic acid. As a result, the reactions over two catalysts have different major products. Water is obtained as the inevitable product during the oxidation reaction. The highly polar acid product, together with water, could be expelled from the hydrophobic surface by a reactant and a solvent, avoiding further oxidation and increasing selectivity. In comparison, water and acids prefer to adsorb on the hydrophilic surface of Pt/AOS, which is disadvantageous to the adsorption on the substrate.

The reaction over Pt/Ph-AOS was little affected by adding water as solvent. As seen in Fig. S14 (ESI†), the conversion of 1-butanol decreased dramatically from 60% without adding water to 25% when 5% water was added over Pt/AOS. In contrast, the activity of Pt/Ph-AOS slightly decreased and high conversion of 1-butanol was still maintained. These results reinforce the importance of the superhydrophobic surface of Pt/Ph-AOS.

Using Pt/Ph-AOS as a catalyst, selective oxidation of other aliphatic alcohols was carried out (Table 1). Ph-AOS is not active in this reaction (entry 1). The catalyst is chemoselective and preferentially oxidizes primary hydroxyl over secondary hydroxyl groups. Aliphatic primary alcohols were converted into acids with high activity (entries 2–8). Secondary alcohols such as 2-octanol and cyclohexanol exhibited low activity (entries 9 and 10), which may be ascribed to the steric hindrance. The catalyst can be simply separated from the reaction solution through centrifugation. After washing with ethanol and drying, it could be repeatedly used at least three times without apparent activity loss (Fig. S15, ESI†). The ICP mass analysis revealed that the Pt content in the reaction solution was only 1.6 ppm, indicating that the catalyst is heterogeneous. The TEM image of the used catalyst shows that the morphology of Pt nanoparticles remains the same as the fresh catalyst, suggesting that Pt particles are stable on catalysts (Fig. S16, ESI†). This high stability is ascribed to a strong binding function of amine groups on the hydrophobic surface.

Table 1 Oxidation of various aliphatic alcohols with Pt/Ph-AOS[a]

Entry	Substrate	Conversion [%]	Selectivity[b] [%]
1[c]	1-Butanol	—	—
2	1-Butanol	98	95
3	Isobutyl alcohol	82	95
4	1-Pentanol	96	92
5	Isoamyl alcohol	89	89
6	1-Hexanol	89	95
7	2-Phenylethanol	69	79
8	1-Octanol	85	93
9	2-Octanol	3	>99
10	Cyclohexanol	32	>99

[a] Reaction conditions: 0.2 mmol alcohol, 0.05 mmol mesitylene, 10 mg Pt/Ph-AOS, 2 mL toluene, 1.0 MPa oxygen, 100 °C, 24 h. [b] The main products were the corresponding acids or ketones for secondary alcohols. Others are aldehyde and esters. [c] Ph-AOS was used as catalyst.

In summary, we have reported a novel superhydrophobic catalyst by supporting Pt nanoparticles on superhydrophobic supports. This study makes us believe that careful tuning of the support wettability to meet reaction requirements will open a new avenue for heterogeneous catalysts.

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12 The surface areas of phenyl groups were calculated based on that the phenyl groups were completely introduced into materials during the preparation process and on the surface of the silica.

13 The hydrophobic index (HI) is defined as the ratio of the adsorbed quantity of benzene vapor to that of water vapor. HI = $V_{\text{benzene}}/V_{\text{Water}}$.