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ARTICLE TYPE

Tuning the wettability of mesoporous silica for enhancing the catalysis efficiency of aqueous reactions

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A series of mesoporous silica-based catalysts with finely-tuned surface wettability have been synthesized, of which the catalysis efficiency towards aqueous hydrogenations is highly dependent on their surface wettability and can be five times higher than that of the commercial Pd/C catalyst.

Using water as reaction solvent is a long-standing goal in view of the fact that all reactions in living systems occur in water, and its unique properties such as low toxicity, non-inflammability, low volatility and high heat capacity.¹ However, most reactions of organic compounds in water proceed sluggishly because their low solubility in water gives rise to the incompatibility of reaction systems and finite reaction interface. Especially in the presence of solid catalysts, the reaction systems often involve three or even four phases. The high mass transport resistance leads to extremely low reaction efficiency. Although addition of co-solvents or surfactants can improve efficiency, these extra additives inevitably brings about troubles in separating and purifying the final products.

Fortunately, it has been found that nano-to-micrometer-sized particles with a suitably wettable surface (interfacial activity) prefer to attach at the oil/water interface, leading to Pickering emulsion [oil-in-water (o/w) or water-in-oil (w/o)].² Pickering emulsion is emerging as an attractive platform for designing efficient aqueous catalysis systems because they can create a large oil/water interface without need for extra additives such as surfactants.³ One of the most key parameters for Pickering emulsion is the surface hydrophobicity/hydrophilicity balance (wettability) of solid catalysts.² Accordingly, to develop efficient methods to control the surface wettability of solid catalysts become crucial to establish efficient Pickering emulsion catalysis systems and to get insights into Pickering emulsion catalysis.

Mesoporous materials featuring high surface area and large pore size have been demonstrated to be versatile supports for loading various metal nanoparticle, metal complex and even

biocatalysts for a wide range of reactions.⁴ The interfacially active mesoporous material-based catalyst is scarcely reported and the method to tune their interfacial activity is unexplored.⁵ We herein develop a facile route to tune the surface wettability of mesoporous silica-based catalysts by controlling the hydrophobization extent of mesoporous silica shell. After depositing Pd nanoparticles on these mesoporous materials, we obtained a set of solid catalysts with finely tuned surface wettability for olefin hydrogenations in pure water. The Pickering emulsion systems formulated with these catalysts show much higher catalysis efficiency than the conventional organic/aqueous biphasic system with conventional mesoporous-silica-based catalyst or the commercial Pd/C catalyst. The catalysis efficiency was found to be strongly dependant on the surface wettability of solid catalysts.

The core-shell-structured mesoporous silica was synthesized through a delayed condensation strategy,⁶ as shown in Fig. 1. This strategy enables the molecular functionality to be positioned region-selectively on the outer shell through a stepwise addition of siliceous precursor. Tetramethyl orthosilicate (TMOS) was used as silicon precursor to construct a core in the presence of cetyltrimethylammonium chloride (CTAC) as template. (MeO)₃Si(CH₂)₇CH₃ (C8) together with TMOS was used to grow a hydrophobic shell. After two steps of hydrolysis and condensation, the desired mesoporous materials were obtained. Pd nanoparticles were introduced onto these materials through adsorption with Pd(OAc)₂ followed by reduction with NaBH₄. After extraction with a hot alcohol solution of NH₄NO₃, a set of solid catalysts Pd/MSS-C_x (*x* represents the molar fraction of (MeO)₃Si(CH₂)₇CH₃ in the total silicon procurers of the second step, varying from 0 to 5%, 10%, 15%, 20% and 25%).

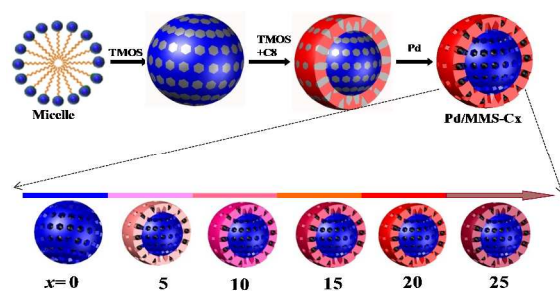


Fig. 1 The preparation process of Pd/MSS-C_x and its structure.

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[†] Electronic Supplementary Information (ESI) available: Experimental section; N₂ sorption analysis; XRD patterns; Solid state NMR spectra; Reaction data. See DOI: 10.1039/b000000x/.

The prepared catalysts are composed of uniform nanospheres. As can be seen from the Fig. 2a, Pd/MSS-C20 shows uniform particles with particle sizes of 200-300 nm. The radially arrayed pores throughout the materials (*ca.* 2 nm) are clearly observed (Fig. 2b). A portion of fine Pd nanoparticles were located inside the nanopores. Pd/MSS-C20 shows a N₂ sorption isotherm close to the type I (Fig. 2c) and possesses a moderate specific surface area (441 m²/g, Table S1, ESI; the N₂ sorption results of other samples are provided in Fig. S1 and Table S1 of ESI). The XRD patterns of the synthesized materials exhibit a diffraction peak centred at 2.5° (Fig. S2, ESI). These results confirm that Pd/MSS-C_x samples possess a structure of typical mesoporous materials. The presence of Q and T bands in the solid state ²⁹Si MAS NMR spectrum of Pd/MSS-C20 indicates that octyl group was linked with the solid materials through co-condensations (Fig. 2c), which is further supported by the ¹³C CP MAS NMR (Fig. S3, ESI) and FT-IR spectra (Fig. S4, ESI). The quantitative results of C contents on this set of solid catalysts confirm that octyl loading gradually increases in the order of Pd/MSS-C0, Pd/MSS-C5, Pd/MSS-C10, Pd/MSS-C15, Pd/MSS-C20 and Pd/MSS-C25, as anticipated. It was interestingly found that water contact angles of these solid catalysts gradually increased from 36° to 42°, 83°, 88°, 102° and 106° as the octyl group loading increased (Fig. 2e). These results confirm that our proposed method allows the catalyst wettability to be finely tunable in a wide range.

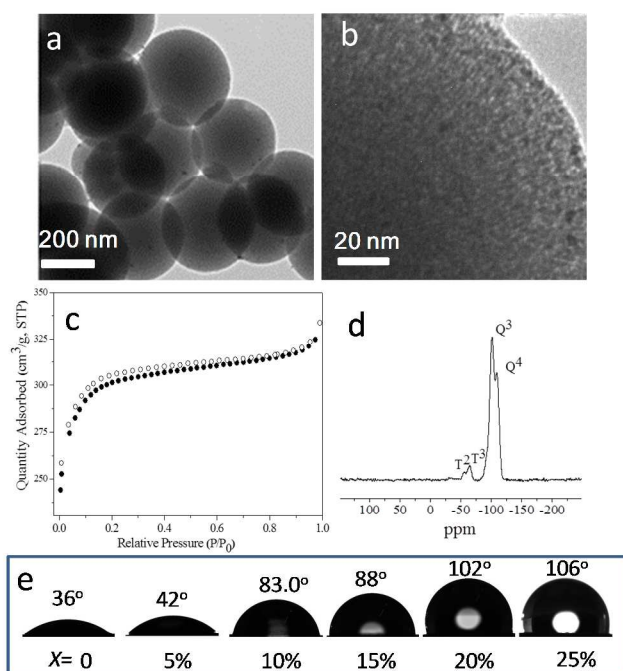


Fig. 2 Characterizations of the prepared catalysts: (a) and (b) TEM images of Pd/MSS-C20; (c) N₂ adsorption-desorption isotherms of Pd/MSS-C20; (d) Solid state ²⁹Si MAS NMR spectrum of Pd/MSS-C20; (e) Water contact angles of Pd/MSS-C0, Pd/MSS-C5, Pd/MSS-C10, Pd/MSS-C15, Pd/MSS-C20 and Pd/MSS-C25.

Hydrogenation is here chosen as a model reaction to examine the catalytic performance of these catalysts in water because it is an important tool for synthesis of various fine chemicals. The hydrogenations were carried out using pure water as reaction medium. After mixing water, olefins and solid catalysts, the reaction system were vigorously stirred (*ca.* 2000 rpm for 3 min)

for emulsification. For Pd/MSS-C0, the reaction system was a conventional two-phase since emulsion droplets were not found with optical microscopy, as shown in Fig. 3. Pd/MSS-C0 particles are mainly distributed in water layer. In contrast, for Pd/MSS-C5, emulsion droplets appeared and their sizes were a range of 400-600 μm. Droplet sizes gradually decreases and then begins to increase. The minimum droplet size is *ca.* 100-250 μm in the case of Pd/MSS-C20.

All hydrogenations were carried out under 0.35 MPa at the stirring input power of 12.5 w. Based on the H₂ uptake rates (Fig. S5, ESI), one can find that these reactions proceed at remarkably different reaction rates. The plot in Fig. 3 quantitatively reflects the change trend of catalysis efficiency T that is calculated before the conversion is less than 30% (catalysis efficiency T means the moles of converted substrate per mole of metal per hour, mol mol⁻¹ h⁻¹). For the conventional biphasic system with Pd/MSS-C0, T is only 727 mol mol⁻¹ h⁻¹. As the octyl loading increases, T gradually increases and reaches the maximum value (2574 mol mol⁻¹ h⁻¹) when the octyl loading is 20%. Further increasing the octyl loading leads to the decrease in catalysis efficiency. More impressively, under the same conditions, the catalysis efficiency of Pd/MSS-C20 is about 5 times higher than the commercial Pd/C catalysts (Fig.S6, ESI).

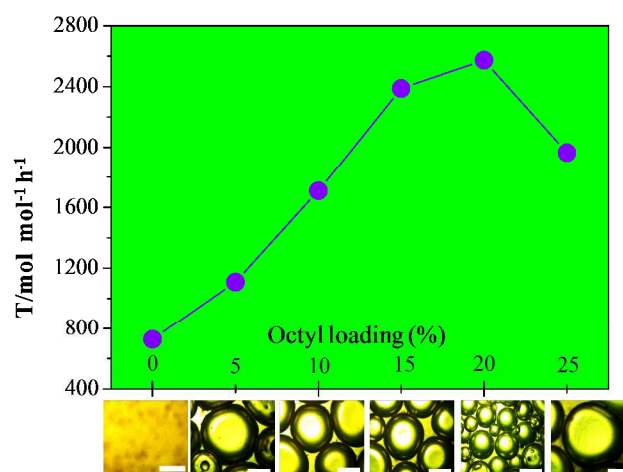


Fig. 3 Catalysis efficiency of the Pickering emulsions formulated with Pd/MSS-C_x (x=0, 5, 10, 15, 20 and 25). Reaction conditions: 10.5 mmol of styrene, 3.1 mL of water, 0.35 MPa of H₂ pressure, 40 °C, solid catalyst containing 0.00292 mmol Pd. The bar is 200 μm.

Obviously, there exist relations between the surface wettability of catalysts, the Pickering emulsion properties and the catalysis efficiency. According to the water contact angle measurement results, Pd/MSS-C0 is too hydrophilic to stabilize Pickering emulsion. Due to the introduction of octyl group, the hydrophobicity of Pd/MSS-C5 is improved, being able to stabilize emulsion although the droplet size is relatively large. As the hydrophobicity further increases, the emulsion droplet size gradually decreases and then begins to increase (Fig. 3). Such results are in good agreement with previous observations that only the particles with moderate wettability can stabilize high-quality Pickering emulsion.⁷ The change tendency of the catalysis efficiency vs droplet size is explained by the fact that the smaller emulsion droplet leads to a larger reaction interface area and the enlarged reaction interface area benefits boosting the catalysis

efficiency (Based on the H₂ uptake rates in Fig. S7 of ESI, it can be estimated that in the pure organic medium the catalysis efficiency of Pd/MSS-C20 is almost equal to that of Pd/MSS-C0, which excludes the possibility that the difference in catalysis efficiency is due to the difference in intrinsic activity of the catalysts). These results also demonstrate that catalytic reaction rate can be rationally controlled through adjusting the surface wettability of the solid catalysts.

The nature of the formulated Pickering emulsion catalysis systems is further reflected by comparison with the conventional biphasic system at different catalyst loadings (Fig. S8, ESI). For the conventional biphasic system with Pd/MSS-C0, the catalysis efficiency dramatically decreases from 772 to 617, 414 mol mol⁻¹ h⁻¹ with increasing the catalyst amount from 1.0 to 1.5, 2.0 wt%. However, for the Pickering emulsion systems with Pd/MSS-C20, its catalyst efficiency has no significant (2303~2574 mol mol⁻¹ h⁻¹) decrease when the catalyst amount is changed from 1.0 to 1.5, 2.0 wt%. These differences are indicative of the fundamental difference in the reaction nature of these two systems. In Pickering emulsion systems, the emulsion droplet size considerably decreases with increasing the catalyst amount (Fig. S9, ESI). The smaller droplet size leads to higher reaction interface area. As a result, the catalyst mass-normalized efficiency has no significant decrease, which is not achievable for the conventional biphasic systems.

We next examined the catalytic performance of Pd/MSS-C20 with other substrates. For all investigated olefins such as styrene, substituted styrene, butyl acrylate, butyl 2-methylacrylate and hexyl 2-methyl acrylate, Pickering emulsions were obtained using these reactants as oil phase, indicating that Pd/MSS-C20 have good interfacial activity towards a wide range of reactants. Under the same conditions, the conversions of all the olefins over Pd/MSS-C20 are much higher than those over Pd/MSS-C0, as reflected by Fig. 4.

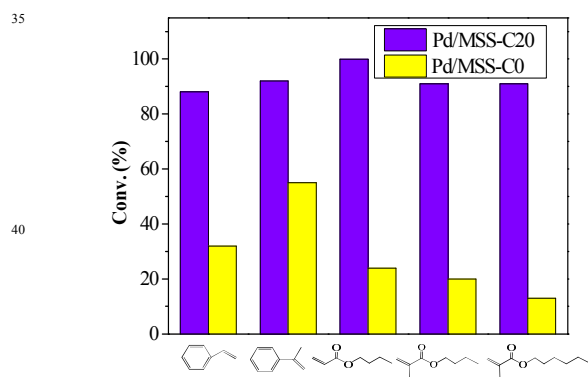


Fig.4 The results of hydrogenation of different substrates in the Pickering emulsion system formulated with Pd/MSS-C20 and the conventional biphasic system in the presence of Pd/MSS-C0. Reaction conditions: 10.5 mmol of styrene, 3.1 mL of water, 0.35 MPa of H₂ pressure, 40 °C, solid catalyst containing 0.00292 mmol Pd. The reaction times correspond to 35, 90, 35, 90, 120 min from left to right.

After completion of the reaction, the catalyst Pd/MSS-C20 was recovered by centrifugation, washed three times with ethanol, dried under vacuum, and then directly reused for the next reaction cycle. In the second to the fifth reaction cycle, emulsion droplets were still observed without any changes in droplet size.

The H₂ consumption rate had no any decrease and the full conversion of styrene was achieved in the second reaction cycle (Fig. S7, ESI).

In summary, a series of interfacially active Pd-supported catalysts are synthesized by introducing octyl groups onto the shell of mesoporous silica through the delayed condensation strategy. Their wettability can be finely tuned by varying the amount of octyl groups. With such interfacially active nanoparticle catalysts, Pickering emulsions can be formulated using various olefins as oil phase. These Pickering emulsion systems show significantly enhanced catalysis efficiency in olefin hydrogenation in comparison to the conventional organic/aqueous biphasic system with the unmodified mesoporous silica-based catalyst and the commercial Pd/C catalyst. Their catalysis efficiency is directly relevant to the surface wettability, which provides a new guide to tune the catalysis efficiency of the reaction using pure water as medium.

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TOC:

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