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Superhydrophobic materials as efficient catalysts for hydrocarbon selective oxidation†

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A new type of superhydrophobic material, FP-Co-SiO_2 was prepared with organic groups immobilized on the surface of the SiO_2-based nanocomposite. This material showed much higher catalytic activity for selective oxidation of hydrocarbons than an equivalent hydrophilic catalyst.

Selective and efficient activation of hydrocarbons and their conversion to valuable building blocks, such as ketones and alcohols, is one of the major scientific challenges.[1] Much effort has been expended to improve the efficiency of catalysts by tuning the active sites or catalytic structures through use of Gif systems,[2] single-site heterogeneous catalyst systems,[3] and other systems.[4] However, little attention has been focused on the reaction components that change during the reaction, which directly affect the interaction between the substrate and catalyst. With the production of oxygen containing organic compounds during the oxidation process, inevitable by-product water molecules increase as the reaction proceeds. Due to the significant differences in polarity and hydrophobicity between water and organic molecules, the competitive adsorption problems caused by the existence of water molecules should not be ignored. Most solid catalysts exhibit hydrophilic properties toward the polar hydroxyl groups or other strong polar groups on the surface, such as metal oxides or functionalized molecular sieves and mesoporous silica. When hydrophilic materials are used as catalysts water molecules that are produced are inclined to be adsorbed on the catalyst's surface rather than the less polar organic substrate, owing to the similar polarity between the catalyst surface and the water molecules. As a result, the effective adsorption of organic substrates is hindered, which might directly affect the conversion.

Recently, superhydrophobic artificial materials (with a water contact angle (CA) higher than 150°), have attracted much attention because of their promising application in various fields.[5] In these applications, the materials' physical properties of self-cleaning and anti-sticking have been primarily utilized in such areas as manufacturing anti-biofouling paints for boats and self-cleaning windshields for automobiles.[5,6] Moreover, superhydrophobic materials have been developed that can efficiently separate water and oil.[7] These applications, in general, have all been limited to the physical domain, while the applications of superhydrophobic materials in chemical reactions have seldom been reported.

In a catalytic reaction, it has been acknowledged that the catalyst's surface properties of hydrophilicity/hydrophobicity could play an important role in its performance.[8] Compared with hydrophobicity, superhydrophobicity is not just the result of the changing quantity of the CA but the changing quality of surface properties. If the surface of a catalyst can be tuned to be superhydrophobic a potentially excellent catalyst for selective hydrocarbon oxidation might be obtained. This is because, with the production of water, the super-strong water repellent ability of the superhydrophobic catalyst assures the timely desorption of a water molecule as soon as it is formed, and then adsorption of the substrate is not hampered. High activity would be expected to be obtained. Reported herein is the preparation of a new kind of superhydrophobic material, as well as the first use of this superhydrophobic material as a highly efficient catalyst for selective hydrocarbon oxidation.

In the present work, the reported superhydrophobic material is a kind of organic group immobilized SiO_2-based nanocomposite, which was prepared through a w/o reverse microemulsion method (ESI †). As shown in Scheme S1,† catalytic active sites were created in the bulk phase by the incorporation of metal ions (red dots). On the surface, hydrophobic organic groups (OG) were immobilized to modify its surface hydrophilicity/hydrophobicity. Using this method, FP-Co-SiO_2 was prepared with cobalt ions in the bulk phase and 3,3,3-trifluoro-propyl (FP) groups on the surface. Transmission electron microscope (TEM) images (Fig. 1a and Fig. 1c) show that these materials are present as nanospheres and the average sizes are about 100 nm for Co-SiO_2 and 160 nm for FP-Co-SiO_2. For the latter, the morphology is different to that of the non-organic groups containing Co-SiO_2. For Co-SiO_2 they exhibit a standard nanosphere morphology with a very slick outerface (Fig. 1b). While a FP-Co-SiO_2 nanosphere looks like a kind of fur ball and the outer part of the nanosphere is fluffy. This difference, which can be more clearly observed in scanning electron microscope (SEM) images (Fig. 1d), was caused by the existence of many trifluoro-propyl groups on the surface of a FP-Co-SiO_2 nanosphere. For the volume effect of the organic groups, the outerparts of the nanospheres did not form a highly condensed SiO_2 network during the preparation process, and then turned fluffy.

As pointed out in the literature,[5] the surface roughness and low surface energy groups are important determining factors for the material's hydrophobicity. In the present work, the surface roughness of these two materials and surface groups was different with the absence of, or in the presence of organic groups. Through sessile water droplet contact angle

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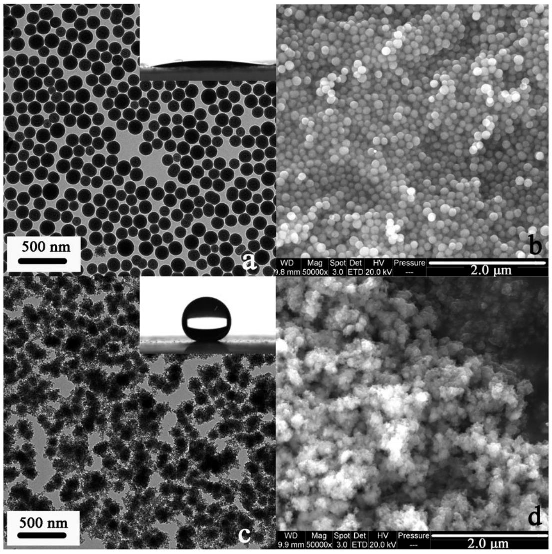

Fig. 1 TEM and SEM images of Co-SiO_2 (a) (b), and FP-Co-SiO_2 (c) (d). (The insets are the images of sessile water droplets on the material film).

measurements it was found that the surfaces of the non-organic group containing Co-SiO_2 were very hydrophilic, with a CA value of below 20°. However, for FP-Co-SiO_2, the increase in surface roughness and the existence of trifluoropropyl groups suggested that this material could show an outstanding hydrophobic behavior. In fact, the CA value reached 154° for FP-Co-SiO_2, which indicated that FP-Co-SiO_2 is a superhydrophobic material.

The existence of organic groups was identified by Fourier transform infrared spectroscopy (FT-IR) and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy measurements (Fig. S1 and S2 in ESI†). The emergence of characteristic peaks associated with the organic groups demonstrated the successful introduction of the organic groups on the material surface. The coordination geometry of cobalt incorporated in the bulk phase was indicated by ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS) (Fig. S3 ESI†). Besides three absorption peaks (525, 583, and 645 nm), which were unambiguously assigned to the $^4A_2$ (F) → $^4T_1$ (P) transition of Co^{2+} ions in a tetrahedral environment, as identified in a previous study, another broad absorption was centered at 356 nm, assigned to a Co^{3+} species.[9] Co^{3+} ions were formed *via* the automatic oxidation of $Co(NH_3)_6{}^{2+}$ by dissolved oxygen during the preparation process. The emergence of Co^{3+} ions was expected, because the high oxidation state transition metal ions act as a key factor in achieving the highest catalytic performance.[10] Formation of a cobalt ammonia complex decreased the standard potential of Co^{3+}/Co^{2+} from 1.84 to 0.1 V, and then high valence state cobalt ions were obtained at ambient temperature, without calcination.

Selective oxidation of ethylbenzene was chosen as a model reaction. When these two materials were used as catalysts, the significant differences in catalytic activity have been obtained (Fig. S4 ESI†). Below 120 °C, hydrophilic Co-SiO_2 was hardly active for this reaction, and conversion of ethylbenzene was only 3.1% at 110 °C. Even when the reaction temperature rose to 130 °C, conversion of ethylbenzene could only reach 13.6%. For the superhydrophobic catalyst, FP-Co-SiO_2, the situation was totally different. At 90 °C, conversion of ethylbenzene was 3.5%, which was higher than that obtained with hydrophilic Co-SiO_2 being used at 110 °C. When the temperature rose to 110 °C, FP-Co-SiO_2 revealed a much higher activity and conversion of ethylbenzene reached 42.2%, which was nearly 14 times that of hydrophilic Co-SiO_2. With a further increase of the reaction temperature, the conversion of ethylbenzene increased to 51.7% and 55.9%, at 120 and 130 °C, respectively.

Using the above materials as catalysts, selective oxidations of other hydrocarbons such as cyclohexene and tetralin were carried out (Table 1). A remarkable difference was observed in the selective oxidation of cyclohexene, where activity of the superhydrophobic material, FP-Co-SiO_2, was higher by a factor of nearly 30 relative to that of the hydrophilic Co-SiO_2 catalyst. For the latter, the conversion was only 2.4%, while it reached 70.4% when FP-Co-SiO_2 was used. Under the same conditions, the conversion of cyclohexene was only about 30% when the homogeneous metal-free catalytic system was used.[11] With tetralin as the substrate, high activity was also obtained when FP-Co-SiO_2 was used, and it was 42.2% higher than the activity obtained with Co-SiO_2. Besides the evident increase observed in conversion, the selectivity for the ketone products also increased. For example, in the selective oxidation of ethylbenzene, the selectivity toward acetophenone was 20.1% when the hydrophilic material, Co-SiO_2, was used as the catalyst. While the selectivity of acetophenone could reach 84.6% when the superhydrophobic

Table 1 Catalytic oxidation of different hydrocarbons over two catalysts[a]

Substrate	Catalyst	Conversion (%)	TON[e]	Selectivity (%)					
Cyclohexene	Co-SiO_2	2.40	349	2-Cyclohexen-1-one	9.4	2-Cyclohexen-1-ol	53.4	Cyclohexenyl hydroperoxide	37.2
	FP-Co-SiO_2[b]	70.1	5894		46.8		32.5	Cyclohexene oxide	9.5
Tetralin[c]	Co-SiO_2	24.0	2169	1-Tetralone	38.2	1-Tetralol	45.7	Tetralin hydroperoxide	9.5
	FP-Co-SiO_2	66.2	3458		54.8		39.8		—
Ethylbenzene[d]	Co-SiO_2	8.30	934	Acetophenone	20.1	Phenylethanol	64.5	Ethylbenzene hydroperoxide	15.4
	FP-Co-SiO_2	51.7	3363		84.6		12.5		2.9

[a] Reaction was carried out with 0.05 g of catalyst in 15 g of hydrocarbon at 353 K for 90 min under 0.3 MPa O_2. [b] The by-products are 1,2-cyclohexandiol, 4-hydroxy-2cyclohexen-1-one, and 2-cyclohexen-1,4-diol. [c] At 373 K. [d] At 393 K for 420 min under 1.0 MPa O_2. [e] Turnover number based on the total cobalt in the material.

FP-Co-SiO_2 was used. In the selective oxidation of hydrocarbons, alcohol is one of the primary oxidation products, which can be further oxidized to a ketone. Higher selectivity for ketones means that superhydrophobic FP-Co-SiO_2 has a stronger oxidation ability, which can also be directly proved by results of the turnover number (TON) comparison. When FP-Co-SiO_2 was used, the TON reached more than 2000 for all situations and could reach 5894 in the selective oxidation of cyclohexene, which is even higher than some homogeneous catalytic system.[11] This kind of catalyst can be simply separated from the reaction solution through centrifugation. After washing with ethanol and drying, it can be repeatedly used for at least three times without a decrease in activity. Based on the above experimental results, we can conclude that the reported superhydrophobic material is an efficient catalyst for the selective oxidation of hydrocarbon.

The special surface property of FP-Co-SiO_2 is believed to be the key factor for obtaining such excellent catalytic performance. In the distribution test (Fig. S5 ESI†), it could be observed that the superhydrophobic FP-Co-SiO_2 could remain in a highly distributed state for a much longer time. The changing trends were monitored through UV-Vis spectroscopy kinetic measurements (Fig. S6 ESI†). In addition, a big difference was found in the adsorbed quantity of hydrophilic water and hydrophobic benzene for these two materials (Table S1 ESI†). Also, the hydrophobicity index (HI) of FP-Co-SiO_2 is 18.7 times as high as that of Co-SiO_2.[12] These results demonstrated that this kind of superhydrophobic material is more oleophilic than the hydrophilic Co-SiO_2 and had better proximity to organic molecules. The formation of water molecules was inevitable during the oxidation reaction process. To imitate this process, a calculated amount of water was put in the bottles (Fig. S5f ESI†). After agitation, it was observed that, for the hydrophilic Co-SiO_2, all the materials were transferred to the water phase. This would consequently affect the adsorption of the organic substrate onto the material surface during the reaction process. For the superhydrophobic FP-Co-SiO_2, however, the situation was totally different and these particles still remained in the organic phase after the addition of water. This meant that the produced water molecules had hardly any effect on the interaction between the catalytically active sites and the substrate molecules because of the super-strong water repellent ability of the material. Accordingly, excellent catalytic performance was obtained when the superhydrophobic FP-Co-SiO_2 was used as the catalyst for selective oxidation of hydrocarbons.

In conclusion, a new kind of superhydrophobic nanocomposite material was prepared with metal ions in the bulk phase and organic groups on the surface. The superhydrophobicity of the material has been demonstrated to improve catalytic performance significantly, which enabled this kind of material to show highly efficient activity in the selective oxidation of hydrocarbons. Due to the inevitable production of water molecules in many kinds of organic reaction, this kind of superhydrophobic material could potentially act as an efficient catalyst for other reactions due to its superhydrophobicity.

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Notes and references

1 (*a*) T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chem. Rev.*, 2005, **105**, 2329; (*b*) J. Piera and J. E. Backvall, *Angew. Chem., Int. Ed.*, 2008, **47**, 3506; (*c*) J. M. Thomas, R. Raja, G. Sankar and R. G. Bell, *Nature*, 1999, **398**, 227; (*d*) H. Frei, *Science*, 2006, **313**, 309.

2 P. Stavropoulos, R. Celenligil-Cetin and A. E. Tapper, *Acc. Chem. Res.*, 2001, **34**, 745.

3 J. M. Thomas, R. Raja and D. W. Lewis, *Angew. Chem., Int. Ed.*, 2005, **44**, 6456.

4 (*a*) R. Palkovits, M. Antonietti, P. Kuhn, A. Thomas and F. Schuth, *Angew. Chem., Int. Ed.*, 2009, **48**, 6909; (*b*) L. Liu, Y. Li, H. B. Wei, M. Dong, J. G. Wang, A. M. Z. Slawin, J. P. Li, J. X. Dong and R. E. Morris, *Angew. Chem., Int. Ed.*, 2009, **48**, 2206; (*c*) J. Tong, L. Bo, Z. Li, Z. Lei and C. Xia, *J. Mol. Catal. A: Chem.*, 2009, **307**, 58.

5 (*a*) T. L. Sun, L. Feng, X. F. Gao and L. Jiang, *Acc. Chem. Res.*, 2005, **38**, 644; (*b*) L. Jiang, Y. Zhao and J. Zhai, *Angew. Chem., Int. Ed.*, 2004, **43**, 4338; (*c*) H. Y. Erbil, A. L. Demirel, Y. Avci and O. Mert, *Science*, 2003, **299**, 1377; (*d*) X. M. Li, D. Reinhoudt and M. Crego-Calama, *Chem. Soc. Rev.*, 2007, **36**, 1350.

6 D. Quere, *Rep. Prog. Phys.*, 2005, **68**, 2495.

7 L. Feng, Z. Y. Zhang, Z. H. Mai, Y. M. Ma, B. Q. Liu, L. Jiang and D. B. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 2012.

8 (*a*) C. Chen, J. Xu, Q. H. Zhang, H. Ma, H. Miao and L. P. Zhou, *J. Phys. Chem. C*, 2009, **113**, 2855; (*b*) S. Klein and W. F. Maier, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2230; (*c*) D. A. Ruddy and T. D. Tilley, *J. Am. Chem. Soc.*, 2008, **130**, 11088; (*d*) A. Salameh, A. Baudouin, J. M. Basset and C. Coperet, *Angew. Chem., Int. Ed.*, 2008, **47**, 2117.

9 (*a*) M. S. Hamdy, A. Ramanathan, T. Maschmeyer, U. Hanefeld and J. C. Jansen, *Chem.–Eur. J.*, 2006, **12**, 1782; (*b*) W. A. Carvalho, P. B. Varaldo, M. Wallau and U. Schuchardt, *Zeolites*, 1997, **18**, 408.

10 R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.*, 1999, **121**, 11926.

11 (*a*) X. L. Tong, J. Xu, H. Miao, G. Y. Yang, H. Ma and Q. H. Zhang, *Tetrahedron*, 2007, **63**, 7634; (*b*) S. K. Jana, Y. Kubota and T. Tatsumi, *J. Catal.*, 2007, **247**, 214; (*c*) J. Y. Qi, H. X. Ma, X. J. Li, Z. Y. Zhou, M. C. K. Choi, A. S. C. Chan and Q. Y. Yang, *Chem. Commun.*, 2003, 1294.

12 (*a*) J. Weitkamp, S. Ernst, E. Roland and G. F. Thiele, *Stud. Surf. Sci. Catal.*, 1997, **105**, 763; (*b*) C. Xu, T. Jin, S. H. Jhung, J. Chang, J. Hwang and S. Park, *Catal. Today*, 2006, **111**, 366.