

Transesterification Catalyzed by Ionic Liquids on Superhydrophobic Mesoporous Polymers: Heterogeneous Catalysts That Are Faster than Homogeneous Catalysts

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S Supporting Information

ABSTRACT: Homogeneous catalysts usually show higher catalytic activities than heterogeneous catalysts because of their high dispersion of catalytically active sites. We demonstrate here that heterogeneous catalysts of ionic liquids functionalized on superhydrophobic mesoporous polymers exhibit much higher activities in transesterification to form biodiesel than homogeneous catalysts of the ionic liquids themselves. This phenomenon is strongly related to the unique features of high enrichment and good miscibility of the superhydrophobic mesoporous polymers for the reactants. These features should allow the design and development of a wide variety of catalysts for the conversion of organic compounds.

Heterogeneous catalysts with good recyclability have been widely applied,^{1–9} but their activities are normally lower than those of homogeneous catalysts because of the lower degree of exposure of active sites to the reactants.^{1–5} This has stimulated the development of strategies for recycling homogeneous catalysts,^{6–8} but recycling is complicated.

Recently, the replacement of homogeneous liquid catalysts by heterogeneous solid catalysts has received much attention because of the recent interest in green or sustainable chemistry for catalyst recovery, operation and anticorrosion in continuous reactors, reactivation, and reuse.^{10–12} In particular, ionic liquids (ILs) supported on porous materials and polystyrene-based polymers are efficient catalysts for the production of fine chemicals and have good recyclability.^{13–18} However, they still have a lower catalytic activity than homogeneous IL catalysts because of the lower degree of exposure of the catalytic sites. In this work, we report that ILs functionalized on superhydrophobic mesoporous polymers, with easy and excellent recyclability, have significantly enhanced catalytic activities in transesterification of tripalmitin with methanol in comparison with the corresponding homogeneous ILs.

Superhydrophobic mesoporous polymers were synthesized by solvothermal copolymerization of divinylbenzene (DVB) with 1-vinylimidazole (vim), 4-vinylpyridine (vpy), or 1-vinyl-2-pyrrolidone (vpr) in ethyl acetate solvent at 100 °C.^{19–22}

After quaternary ammonization and anion-exchange treatment, ILs functionalized on the polymers were obtained (Table S1 in the Supporting Information). Figure 1A shows the synthesis of

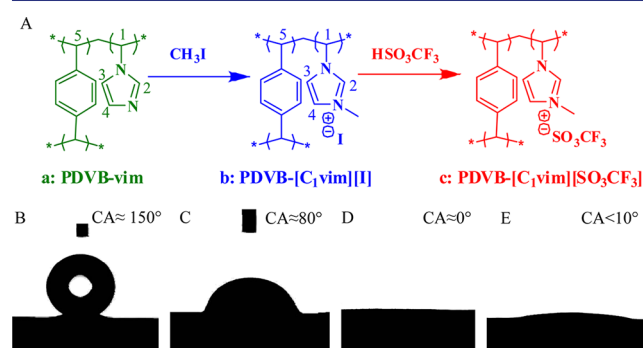


Figure 1. (A) Scheme for the synthesis of PDVB-[C₁vim][SO₃CF₃] from PDVB-vim. (B, C) Contact angle for a water droplet on the surface of (B) PDVB-vim and (C) PDVB-[C₁vim][SO₃CF₃]. (D, E) Contact angle of a droplet of (D) methanol and (E) tripalmitin on the surface of PDVB-[C₁vim][SO₃CF₃].

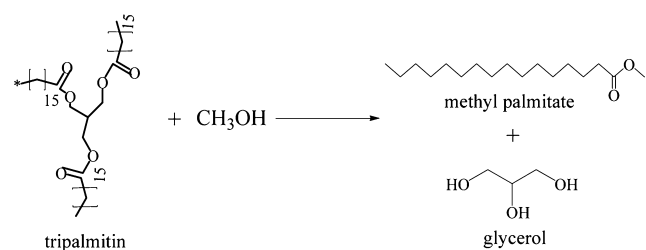
the copolymer of divinylbenzene with vim (PDVB-vim), quaternary ammonization of PDVB-vim with CH₃I (PDVB-[C₁vim][I]), and formation of the SO₃CF₃⁻ anion-functionalized mesoporous copolymer PDVB-[C₁vim][SO₃CF₃]. These samples exhibit type-IV N₂ sorption isotherms with hysteresis loops at relative pressures of 0.7–0.9 (Figure S1A and Table S2), indicating the presence of mesoporosity, which was confirmed by transmission electron microscopy (Figure S2). Correspondingly, their pore sizes are distributed at 10–40 nm (Figure S1B). The Brunauer–Emmett–Teller (BET) surface areas and pore volumes of PDVB-vim, PDVB-[C₁vim][I], and PDVB-[C₁vim][SO₃CF₃] are 670, 592, and 181 m²/g and 1.13, 1.06, and 0.75 cm³/g, respectively (Table S2). In addition, the ¹³C NMR spectrum of PDVB-vim shows peaks at 137 and 116 ppm (Figure S3), which are assigned to the carbon atoms in the imidazolate ring.²⁰ The IR spectrum of PDVB-[C₁vim]-

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[SO₃CF₃] shows bands at 642, 1032, and 1170 cm⁻¹ (Figure S4), which are attributed to the presence of S–O and C–F bonds.²³ X-ray photoelectron spectroscopy measurements of PDVB-[C₁vim][SO₃CF₃] (Figures S5 and S6) show a S 2p peak at 169.1 eV associated with the S–O bond; C 1s peaks at 284.8, 286.3, and 291.9 eV associated with C–C, C–N, and C–F bonds, respectively; and N 1s peaks at 402.0 and 399.9 eV associated with N–C bonds. These data are in good agreement with the presence of [C₁vim][SO₃CF₃] in the sample.²⁴ When a water droplet was brought in contact with the surface of PDVB-vim, the contact angle (CA) was measured to be 150° (Figure 1B), indicating that PDVB-vim is superhydrophobic. For a water droplet on the surface of PDVB-[C₁vim][SO₃CF₃], the CA was measured to be 80° (Figure 1C). However, the CA is zero for a water droplet in contact with the surface of SBA-15-[C₁vim][SO₃CF₃] (Figure S7). These results suggest that PDVB-[C₁vim][SO₃CF₃] is relatively hydrophobic in comparison with SBA-15-[C₁vim][SO₃CF₃]. This conclusion was confirmed by water adsorption (Figure S8). When a droplet of methanol or tripalmitin was allowed to contact the surface of PDVB-[C₁vim][SO₃CF₃], the CA was close to zero (Figure 1D and E), indicating the superwettability for methanol and tripalmitin. Furthermore, thermogravimetric analysis showed that PDVB-[C₁vim][SO₃CF₃] has superior thermal stability, with decomposition starting at 365 °C (Figure S9), which is even higher than for Nafion NR50 (330 °C), one of the most stable resins.

Table 1 presents data for various catalysts in the transesterification of tripalmitin, which has been widely investigated for the production of biodiesel.²⁵ Notably, the heterogeneous catalysts consisting of ILs functionalized on PDVB supports (entries 1–6) showed much higher activities than the homogeneous [C₁vim][SO₃CF₃] IL catalyst (entry 7) and

Table 1. Activities in Transesterification of Tripalmitin with Methanol over Various Catalysts^a



entry	catalyst	yield of methyl palmitate (%)
1	PDVB-[C ₁ vim][SO ₃ CF ₃]	96.9
2	PDVB-[C ₃ vim][SO ₃ CF ₃]	>99.9
3	PDVB-[C ₄ vim][SO ₃ CF ₃]	97.4
4	PDVB-[C ₃ vpy][SO ₃ CF ₃]	99.5
5	PDVB-[C ₄ vpy][SO ₃ CF ₃]	92.9
6	PDVB-[C ₃ vpr][SO ₃ CF ₃]	99.3
7 ^b	[C ₁ vim][SO ₃ CF ₃]	89.1
8	SBA-15-[C ₁ vim][SO ₃ CF ₃]	24.1
9	Amberlyst 15	28.6
10 ^c	PDVB-[C ₁ vim][SO ₃ CF ₃]	93.5
11 ^c	PDVB-[C ₃ vim][SO ₃ CF ₃]	98.1
12 ^c	Amberlyst 15	20.2

^aConditions: 0.05 g of catalyst, 1.04 mmol of tripalmitin, 92.7 mmol of methanol, 65 °C, 16 h. ^bThe same number of catalytic sites as those in PDVB-[C₁vim][SO₃CF₃]. ^cFifth run to test the reusability of the catalyst.

conventional heterogeneous catalysts consisting of SBA-15-supported [C₁vim][SO₃CF₃] (entry 8) and the acidic resin Amberlyst 15 (entry 9). For example, the heterogeneous catalyst PDVB-[C₁vim][SO₃CF₃] showed a 96.9% yield of palmitate (entry 1), which is higher than that of the homogeneous catalysts [C₁vim][SO₃CF₃] itself (89.1%; entry 7).

Heterogeneous catalysts generally exhibit much lower activities than homogeneous catalysts because the degree of exposure of the catalytically active sites to reactants is much lower over heterogeneous catalysts than over homogeneous catalysts.^{1–4} However, the heterogeneous catalyst PDVB-[C₁vim][SO₃CF₃] exhibited a higher activity than the homogeneous catalyst [C₁vim][SO₃CF₃] with the same number of active sites. This unique phenomenon is attributed to the contribution of the PDVB-vim support. To understand the role of the PDVB-vim support in catalysis, we measured the adsorption kinetics of methanol and tripalmitin on PDVB-[C₁vim][SO₃CF₃] (Figure 2) and found that the methanol and

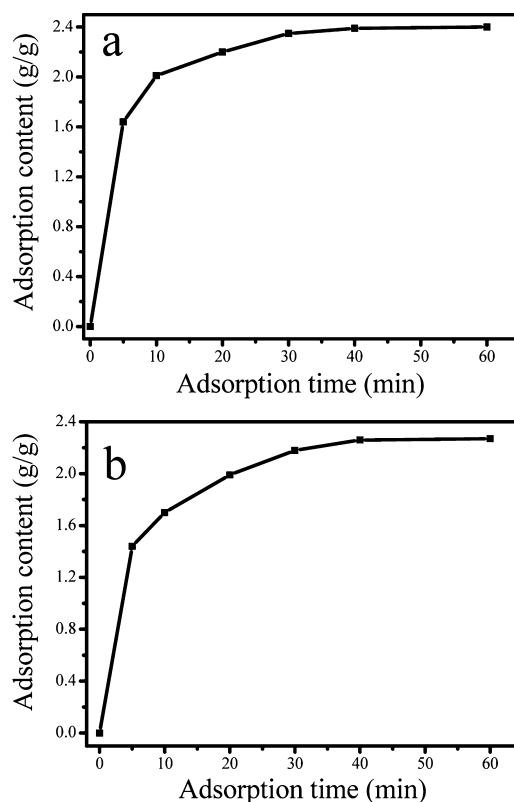


Figure 2. Adsorption kinetics of (a) methanol and (b) tripalmitin on the PDVB-[C₁vim][SO₃CF₃] catalyst.

tripalmitin reactants in the transesterification reaction can be remarkably adsorbed on the catalyst because of its superwettability for the reactants (Figure 1D,E). In addition, the competitive adsorption studies showed that adsorption of the reactants is more competitive than that of products in this reaction (Figures S10 and S11). Contact angle tests showed that the products, methyl palmitate and glycerol, have higher contact angles (Figure S12) than the reactants on PDVB-[C₁vim][SO₃CF₃] (Figure 1D,E), indicating that the reactants have much better wettability than the products. These results mean that the reactants in the transesterification can be enriched in PDVB-[C₁vim][SO₃CF₃] (Figure S13). The

increase in the reactant concentration in the catalyst leads to an enhancement of the activity,¹ in good agreement with the reactant enrichment in carbon nanotube catalysts.²⁶

It is also interesting to note that the ILs functionalized on the PDVB-vim support showed very good recyclability (Table 1, entries 10 and 11). For example, there was almost no activity loss over PDVB-[C₁vim][SO₃CF₃] after recycling four times (entry 11). This might be associated with the stable polymer network (Figure S9 and Table S2). In contrast, after the same number of recycles, the activity over Amberlyst 15 was remarkably reduced from 28.6 to 20.2% (entry 12; also see Table S2). The excellent recyclability of the catalysts is potentially important for industrial applications.

We extended the use of PDVB-[C₁vim][SO₃CF₃] to the Peckmann reaction (Table S3), the Kharasch addition (Table S3), the esterification of cyclohexanol with acetic acid (Table S4), and the hydration of propylene oxide (Table S4). The results showed that the heterogeneous catalyst PDVB-[C₁vim]-[SO₃CF₃] is still much more active than the homogeneous catalysts [C₁vim][SO₃CF₃] and H₂SO₄ with the same number of active sites (Table S3 and S4) as a result of the high enrichment and good miscibility of the superhydrophobic mesoporous polymers for the reactants (Figure S13 and Figure S14).

In summary, ILs functionalized on superhydrophobic mesoporous polymers, such as PDVB-[C₁vim][SO₃CF₃], were successfully prepared and found to exhibit even higher activities in a series of catalytic reactions such as transesterification, the Peckmann reaction, Kharasch addition, esterification, and hydration than the corresponding homogeneous ILs. This feature should be important in the future for the design and preparation of heterogeneous catalysts with both high activity and good recyclability.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Gates, B. C. *Catalytic Chemistry*; Wiley: New York, 1992.
- (2) (a) De Vos, D. E.; Dams, M.; Sels, B. F.; Jacobs, P. A. *Chem. Rev.* **2002**, *102*, 3615. (b) Fu, Q.; Li, W.-X.; Yao, Y.; Liu, H.; Sun, H.; Ma, D.; Gu, X.; Chen, L.; Wang, Z.; Zhang, H.; Wang, B.; Bao, X. H. *Science* **2010**, *328*, 5982. (c) Huang, J.; Jiang, T.; Gao, H.; Han, B. X.; Liu, Z. M.; Wu, W. Z.; Chang, Y. H.; Zhao, G. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 1397.
- (3) (a) Climent, M. J.; Corma, A.; Iborra, S. *Chem. Rev.* **2011**, *111*, 1072. (b) He, L.; Wang, J.-Q.; Gong, Y.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Angew. Chem., Int. Ed.* **2011**, *50*, 10216. (c) Wan, Y.; Wang,

H. Y.; Zhao, Q. F.; Klingstedt, M.; Terasaki, O.; Zhao, D. Y. *J. Am. Chem. Soc.* **2009**, *131*, 4541.

- (4) (a) Dioumaev, V. K.; Bullock, R. M. *Nature* **2003**, *424*, 530. (b) Ji, N.; Zhang, T.; Zheng, M.; Wang, A.; Wang, H.; Wang, X.; Chen, J. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 8510. (c) Wang, L.; Meng, X.; Wang, B.; Chi, W.; Xiao, F.-S. *Chem. Commun.* **2010**, *46*, 5003.
- (5) Gladysz, J. A. *Chem. Rev.* **2002**, *102*, 3215.
- (6) Cole-Hamilton, D. J. *Science* **2003**, *299*, 1702.
- (7) (a) Shylesh, S.; Schuenemann, V.; Thiel, R. W. *Angew. Chem., Int. Ed.* **2010**, *49*, 3428. (b) Xiang, S.; Zhang, Y. L.; Xin, Q.; Li, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 821.
- (8) (a) Xi, Z.-W.; Zhou, N.; Sun, Y.; Li, K.-L. *Science* **2001**, *292*, 1139. (b) Xing, R.; Liu, N.; Liu, Y. M.; Wu, H. H.; Jiang, Y. W.; Chen, L.; He, M. Y.; Wu, P. *Adv. Funct. Mater.* **2007**, *17*, 2455.
- (9) Liu, H. Z.; Jiang, T.; Han, B. X.; Liang, S. G.; Zhou, Y. X. *Science* **2009**, *326*, 5957.
- (10) (a) Busca, G. *Chem. Rev.* **2007**, *107*, 5366. (b) Deng, W. P.; Liu, M.; Zhang, Q. H.; Tan, X. S.; Wang, Y. *Chem. Commun.* **2010**, *46*, 2668. (c) Wongsiriwan, U.; Noda, Y.; Song, C. S.; Prasassarakich, P.; Teboah, Y. *Energy Fuels* **2010**, *24*, 3232.
- (11) Corma, A.; Garcia, H. *Chem. Rev.* **2003**, *103*, 4307.
- (12) (a) Huang, J.-F.; Luo, H.; Liang, C.; Sun, I.-W.; Baker, G. A.; Dai, S. *J. Am. Chem. Soc.* **2005**, *127*, 12784. (b) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- (13) Parvulescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, *107*, 2615.
- (14) Kim, D. W.; Chi, D. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 483.
- (15) Leng, Y.; Wang, J.; Zhu, D. R.; Ren, X. Q.; Ge, H. Q.; Shen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 168.
- (16) Sievers, C.; Jimenez, O.; Muller, T. E.; Steuernagel, S.; Lercher, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 13990.
- (17) Jin, M.-J.; Taher, A.; Kang, H. J.; Choi, M.; Ryoo, R. *Green Chem.* **2009**, *11*, 309.
- (18) Shi, F.; Zhang, Q.; Li, D.; Deng, Y.-Q. *Chem.—Eur. J.* **2005**, *11*, 5279.
- (19) Liu, F. J.; Li, W.; Sun, Q.; Zhu, L.-F.; Meng, X.-J.; Guo, Y.-H.; Xiao, F.-S. *ChemSusChem* **2011**, *4*, 1059.
- (20) Pretula, J.; Kaluzynski, K.; Penczek, S. *Macromolecules* **1986**, *19*, 1797.
- (21) Liu, F. J.; Meng, X.-J.; Zhang, Y.-L.; Ren, L.-M.; Nawaz, F.; Xiao, F.-S. *J. Catal.* **2010**, *271*, 52.
- (22) Zhang, Y.-L.; Wang, J.-N.; He, Y.; He, Y.-Y.; Xu, B.-B.; Wei, S.; Xiao, F.-S. *Langmuir* **2011**, *27*, 12585.
- (23) Scaranto, J.; Charmet, A. P.; Giorgianni, S. *J. Phys. Chem. C* **2008**, *112*, 9443.
- (24) Kolbeck, C.; Killian, M.; Maier, F.; Paape, N.; Wasserscheid, P.; Steinruck, H.-P. *Langmuir* **2008**, *24*, 9500.
- (25) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044.
- (26) Chen, Z. J.; Guan, Z. H.; Li, M. R.; Yan, Q. H.; Li, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 4913.

■ NOTE ADDED AFTER ASAP PUBLICATION

The structure of PDVB in Figure 1A was incomplete in the version published ASAP September 28, 2012. The corrected version was reposted on October 3, 2012.