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Bifunctionalized Hollow Nanospheres for the One-Pot Synthesis of Methyl Isobutyl Ketone from Acetone

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Pd-doped propyl sulfonic acid-functionalized hollow nanospheres proved to be efficient bifunctionalized catalysts for the one-pot synthesis of methyl isobutyl ketone (MIBK) from acetone and hydrogen in liquid phase. These hollow nanospheres exhibited a higher activity than their bulk mesoporous counterparts (SBA-15 or FDU-12), mainly due to the short diffusion resistance of hollow nanospheres. Hollow nanospheres with silica frameworks showed higher activity and selectivity for MIBK than those with ethane-bridged frameworks, suggesting that hollow nanospheres with hydrophilic surface properties

Introduction

Methyl isobutyl ketone (MIBK), as an important fine chemical, has been widely used as solvent for paint and protective coatings. Traditionally, MIBK is manufactured through a three-step process involving the base-catalyzed aldol condensation of acetone to diacetone alcohol (DA), the acid-catalyzed dehydration of DA to mesityl oxide (MO), and the metal-catalyzed hydrogenation of MO to MIBK.^[1] The use of homogeneous acid and base catalysts causes pollution and corrosion problems. Heterogeneous multifunctional catalysts, which contain acidbase and metal active sites,^[2] are capable of performing all three reactions in one step without separating the intermediates of DA and MO and have attracted considerable interest. In the one-step synthesis of MIBK, side reactions, such as the acid-base catalyzed condensation of acetone, the deep condensation of MIBK, and the hydrogenation of acetone should be avoided to increase the yield of MIBK.

Numerous bifunctional catalysts have been studied in onestep syntheses of MIBK in both the gas and liquid phase; for example, Pd supported on acidic or basic solids, ZSM-5,^[2a] MIL-101,^[2b] polyoxometalates,^[2c] resins,^[2d] Nb₂O₅/silica^[2e] and hydrotalcites.^[2f] For most reported one-step processes for the production of MIBK catalyzed by solid catalysts, the conversion of acetone was kept under 50% to guarantee high selectivity for MIBK, given that MIBK would react with acetone yielding unwanted byproducts, such as diisobutyl ketone (DIBK) and isopropanol (IP). Because acetone is hydrophilic, whereas MIBK is relatively hydrophobic, it is not surprising that the hydrophilicity/hydrophobicity of the solid catalyst would have a significant impact on the activity and selectivity for MIBK, by influencing the diffusion rates of the two compounds. However, the influence of surface properties of the catalysts on their catalytic performance is seldom reported in one-pot syntheses of MIBK. favor the formation of MIBK. This is probably due to the increased affinity of the hydrophilic surface towards acetone and its decreased affinity towards MIBK, which precludes deep condensation of MIBK with acetone. Under optimal conditions, up to 90% selectivity for MIBK can be obtained with conversions of acetone as high as 43%. This result is among the best reported so far for mesoporous silica-based catalysts. The control/fine-tuning of morphology and surface properties provides an efficient strategy for improving the catalytic performance of solid catalysts.

The morphology of the solid catalysts may have considerable influence on their catalytic performance. In the past decade, nanoparticles have attracted much attention as excellent catalysts due to short diffusion lengths as a result of particle size.^[3] Hollow nanospheres, a special type of nanoparticles, have low densities, as well as high thermal and mechanical stabilities, representing a promising catalytic material. Kim et al. reported that hollow Pd spheres exhibited good catalytic activities in Suzuki cross-coupling reactions and can be reused many times without loss of catalytic activity.[3e] The same group used CuO hollow nanostructures to catalyze cycloadditions of azides with terminal alkynes to provide the products in good yields.^[3d] Recently, we found that silica hollow nanospheres functionalized with chiral groups are efficient solid chiral catalysts for asymmetric reactions.^[3b,c] Despite these advancements, the design and synthesis of hollow nanospheres for catalysis are still under development.

Herein, we report the synthesis of sulfonic acid-functionalized hollow nanospheres with different surface hydrophilicity/ hydrophobicity by using a soft-templating strategy. These hollow nanospheres in combination with Pd are efficient solid

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catalysts for the one-pot synthesis of MIBK from acetone in the liquid phase. The influence of surface properties and morphology of the solid catalysts on catalytic performance is investigated.

Results and Discussion

Characterization

With an aim to investigate the influence of surface properties on the catalytic performance of the solid catalysts in the onepot synthesis of MIBK, sulfonic acid-functionalized hollow nanospheres with different surface properties were prepared by using 1,2-bis(trimethoxysilyl)ethane (BTME) and tetramethoxysilane (TMOS) as silane precursors for the construction of the hollow nanosphere network. The soft-template strategy was used to fabricate the hollow nanospheres. The single surfactant micelle (F127) was formed at low surfactant concentration with the aid of a salting-out inorganic electrolyte (NaOAc), and the assembly of BTME around the single surfactant micelle led to the formation of organic-inorganic hybrid hollow nanospheres.^[4b] The sulfonic acid-functionalized SBA-15 (SO₃H-SBA-15) and FDU-12 (SO₃H-FDU-12) were also synthesized to investigate the influence of morphology on the catalytic performance of solid catalysts.

Figure 1 displays TEM images of sulfonic acid-functionalized hollow spheres with ethane-bridged frameworks ($30 SO_3H$ -E-HS) and their counterparts with silica frameworks (SO_3H -Si-HS).



Figure 1. TEM images of sulfonic acid-functionalized organic–inorganic hybrid hollow nanospheres: a) 30 SO₃H-E-HS and b) SO₃H-Si-HS.

The TEM images confirm that both $30 \text{ SO}_3\text{H}$ -E-HS and SO_3H -Si-HS are hollow nanospheres. From the TEM images, we estimate that $30 \text{ SO}_3\text{H}$ -E-HS and SO_3H -Si-HS particles are 14–15 nm in size with an inner void of about 10 nm. The shell thickness is in the range of 4–5 nm. All $n \text{ SO}_3\text{H}$ -E-HS and SO_3H -Si-HS samples show typical type IV isotherms with two capillary condensation steps, suggesting that these samples have two types of mesopores^[4] (the primary and secondary mesopores are from the core and the aggregated nanospace of the hollow nanospheres, respectively; see the Supporting Information, Figures S1 and S2). The Brunauer–Emmett–Teller (BET) surface area of $n \text{ SO}_3\text{H}$ -E-HS decreased from 825 to 472 m²g⁻¹ with the S content increasing from 0.84 to 2.47 mmolg⁻¹. SEM and TEM images show that SO₃H-SBA-15 and SO₃H-FDU-12 are composed of rods, which are of 150–200 nm in width, and irregu-

larly shaped microparticles with sizes of $3-8 \mu m$, respectively (see the Supporting Information, Figures S3 and S4). Nitrogen adsorption–desorption isotherms confirmed that SO₃H-SBA-15 and SO₃H-FDU-12 have typical type IV traits with H1 and H2 hysteresis loops, respectively (see the Supporting Information, Figure S5).

Cross polarization and magic angle spinning (CPMAS) ¹³C NMR spectra of *n* SO₃H-E-HS clearly show that the resonance at 5.8 ppm can be assigned to carbon atoms of bridging ethylene, whereas the resonances at 16, 19, and 54.5 ppm correspond to the ³C, ²C, and ¹C carbon atoms of \equiv Si-¹CH₂²CH₂³CH₂-SO₃H, respectively (Figure 2).^[3b] The signal at 69.3 ppm is probably due to the carbon atoms of O-CH₂CH₃ formed during the surfactant extraction process. No signals in the range of 90–110 ppm were observed in ²⁹Si NMR spectra of nSO₃H-E-HS, confirming the integrity of the organic groups in n SO₃H-E-HS. The signals at -65.2 and -59.2 ppm are from the T^3 [SiC(OSi)₃] and T^2 [Si(OH)C(OSi)₂] silicon atoms connected with the organic groups. NMR characterization confirmed the successful incorporation of ethylene and propyl sulfonic acid groups in the hollow nanospheres. The acidity of the hollow nanospheres increased from 0.41 to 1.33 mmol g⁻¹ from 10 SO₃H-E-HS to 40 SO₃H-E-HS (Table 1). The hollow nano-



Figure 2. a) CPMAS ¹³C and b) MAS ²⁹Si NMR spectra of n SO₃H-E-HS (from top to bottom): 10 SO₃H-E-HS, 20 SO₃H-E-HS, 30 SO₃H-E-HS, and 40 SO₃H-E-HS.

Table 1. Physical and textural properties, elemental analyses and acid exchange capacities of sulfonic acidfunctionalized materials.

	S_{BET}^{M} [m ² g ⁻¹]	Pore volume ^{ıbj} [cm³g ⁻¹]	Pore diameter ^{ici} [nm]	Amount of acid sites ^[d] [mmol g^{-1}]
10 SO ₃ H-E-HS	825	1.48	6.6, 19.7	0.41
20 SO ₃ H-E-HS	739	1.30	6.5, 19.2	0.87
30 SO ₃ H-E-HS	522	1.01	6.5, 16.7	1.16
40 SO₃H-E-HS	472	0.80	6.3, 16.1	1.33
SO₃H-Si-HS	429	1.99	9.6, 39.8	1.06
SO₃H-SBA-15	768	0.71	6.5	1.16
SO ₃ H-FDU-12	423	0.47	12.9	1.31

[a] BET surface area. [b] Total pore volume determined at a relative pressure of 0.99. [c] Calculated from the adsorption branch by the Barrett–Joyner–Halenda (BJH) method. [d] Determined by ion exchange and titration.

spheres with a silica framework (sulfonic acid-functionalized SBA-15 and FUD-12) had an acidity and BET surface area comparable to 30 SO₃H-E-HS. The positions of Pd species deposited on the spheres were characterized by TEM and angular dark field scanning transmission electron microscopy (DFSTEM) imaging. Pd nanoparticles with sizes of 2–5 nm were immobilized on the external surface of hollow nanospheres (see the Supporting Information, Figure S7).

cantly more active than Pd/Amberlite 120 (acidity of 4.4 mmol g⁻¹). This is due to the high surface area of the hollow nanospheres, which can facilitate the accessibility of the acidic sites to the reactants and the fast diffusion rate of the reactant and products during the catalytic process.

It seems that a synergetic effect between two acid sites of the hollow nanospheres exists. A similar phenomenon was reported by Davis et al.^[6] They found that two organic alkylsulfonic acid groups in close proximity on the silica surface,

One-step synthesis of MIBK

The one-step selective conversion of acetone into MIBK involves the condensation of acetone (catalyzed by acid/base) for the formation of MO, followed by hydrogenation of MO to produce MIBK (Scheme 1). The synergism of the acid/base and metal nanoparticles is needed for this cascade reaction. Pd is chosen as the metal catalyst for the hydrogenation because it is highly selective in the hydrogenation of C=C.^[5]

Table 2 summarizes the results of one-pot syntheses of MIBK catalyzed by different types of sulfonic acid-functionalized materials. In the presence of Pd/ SO₃H-E-HS, the reaction proceeds smoothly to afford conversions of 10.1-43.4% with a selectivity for MIBK in the range of 78.9-86.2%. The conversion goes parallel with the acidity of the solid catalysts. MIBK selectivity increases with the increase in solid catalyst acidity and is maximized for Pd/20SO₃H-E-HS. The selectivity for DIBK (deep condensation product of MIBK with



Scheme 1. Main reaction pathways in the acetone condensation process.^[2b]

Catalyst Acid site density ^[b] Conversion Selectivity [%]							мо	othor
		[70]			C3	IF		other
Pd/10SO₃-E-HS	0.3	10.1	78.9	1.3	2.1	13.5	0.1	4.1
Pd/20 SO₃-E-HS	0.7	28.3	88.6	2.8	2.2	5.6	0.1	0.7
Pd/30 SO₃-E-HS	1.3	36.1	86.2	4.9	3.2	4.9	0.1	1.7
Pd/40 SO₃-E-HS	1.7	43.4	83.2	7.1	2.1	3.8	0.2	3.6
Pd/SO₃H-Si-HS	1.4	43.1	90.7	3.7	2.0	1.4	0	2.2
Pd/SO₃H-FDU-12	1.9	35.1	86.6	1.6	6.8	3.4	0	1.6
Pd/SO ₃ H-SBA-15	1.2	34.1	89.8	3.1	3.7	1.8	0	1.6
Pd/Amberlite 120	-	18.1	89.0	1.1	2.8	3.3	1.1	2.8

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acetone on acid sites) and IP (hydrogenation product of acetone) increases and decreases, respectively, with the increase in solid catalyst acidity. The above results suggest that high acidity favors the conversion of acetone and suppresses the hydrogenation of acetone (side reaction). However, high acidity levels decrease the selectivity for MIBK probably because the deep condensation of MIBK with acetone is favored. Also, Pd/20 SO₃H-E-HS and Pd/30 SO₃H-E-HS are signifitested in the condensation of phenol and acetone to yield Bisphenol A, exhibited twice the activity per acid site relative to conventional alkylsulfonic acid-modified SBA-15 materials. Considering that the density of acid sites in $40 \text{ SO}_3\text{H-E-HS}$ (1.7 acid sites per nm²) is about six times that of $10 \text{ SO}_3\text{H-E-HS}$ (0.3 acid sites per nm²), the propyl sulfonic acid sites in the former are more likely to cooperate relative to those in $10 \text{ SO}_3\text{H-E-HS}$. Thus, the activity increases in parallel with the acidity (Figure 3).



Figure 3. Polynomial regression of activity versus acidity, $Y = 5.1 X^2 + 25.6 X - 0.3$, $R^2 = 0.996$, where Y and X refer to conversion and acidity, respectively.

To confirm the cooperative effect of the sulfonic acid groups, the activities of $10SO_3H$ -E-HS and $40SO_3H$ -E-HS are compared under the same substrate-to-catalyst ratio. $40SO_3H$ -E-HS is twice as active as $10SO_3H$ -E-HS and exhibits higher selectivity for MIBK than $10SO_3H$ -E-HS (Table 3). This suggests that the sulfonic acid groups in high density are likely to bind

Table 3. Influence of density of acid sites on the synthesis of MIBK. ^[a]								
Catalysts	Conversion [%]	vity [%] DIBK	C3	IP	МО	others		
Pd/10 SO₃H-E-HS Pd/40 SO₃H-E-HS	10.1 20.6	78.9 90.3	1.3 5.3	2.1 1.0	13.5 2.4	0.1 0	4.1 1.0	
[a] Reaction conditions are the same as in Table 2 except that acid amounts used in the reactions were identical. 200 mg of $10 \text{ SO}_3\text{H-E-HS}$ and 61.6 mg of $40 \text{ SO}_3\text{H-E-HS}$ were used in this reaction.								

together to inhibit their interaction with surface silanol groups and promote lateral interactions between adjacent groups.^[6a] So the acid strength was also enhanced for 40SO₃H-E-HS due to the high density of sulfonic acid groups.

The deep condensation of MIBK with acetone is the major side reaction in the one-pot synthesis of MIBK. The reactant (acetone) and product (MIBK) have a slight difference in polarity. Therefore, the influence of hydrophilicity/hydrophobicity of the nanospheres on their catalytic performance was investigated using Pd/SO₃H-Si-HS and Pd/30SO₃H-E-HS with similar densities of acidic sites and physical parameters as model catalysts. Under similar reaction conditions, Pd/SO₃H-Si-HS exhibited higher conversions and higher selectivity for MIBK than Pd/ 30SO₃H-E-HS (Table 2). The surface properties of the two samples were investigated by measuring water vapor adsorption at 298 K (Figure 4a). It is not necessary for a hydrophilic material to have a high water sorption capacity, whereby the water



Figure 4. a) Water and b) acetone adsorption isotherms of hollow nanospheres (\bullet : SO₃H-Si-HS; **=**: 30 SO₃H-E-HS).

sorption capacity is mainly determined by the pore volume of the materials. According to Mintova et al., among others,^[7] hydrophobicity is defined as the low affinity of a sorbent to water. It was proposed that the slope of the water sorption isotherm at "zero loading" should be used as an indicator for hydrophobicity classification. Using this definition, the sorbent that shows a steep slope in water sorption isotherms is defined as a hydrophilic sorbent. In the high relative pressure range, the adsorption behavior is determined by the pore structure of the materials, not the hydrophilicity of the surface. We thus compared water adsorption capacities at the low relative pressure range ($P/P_0 \leq 0.30$). As expected, the hollow acid spheres with the silica framework showed a sharper adsorption isotherm than $30 \text{ SO}_3\text{H-E-HS}$ (with ethylene groups in the network). The above results suggested that $\text{SO}_3\text{H-Si-HS}$ had a more hydrophilic surface. We also measured the acetone vapor adsorption on $\text{SO}_3\text{H-Si-HS}$ and $30 \text{ SO}_3\text{H-E-HS}$ (Figure 4 b). Similar to the results of water adsorption, $\text{SO}_3\text{H-E-HS}$ (Figure 4 b). Similar to the results of water adsorption, $\text{SO}_3\text{H-E-HS}$ exhibited a higher acetone adsorption than $30 \text{ SO}_3\text{H-E-HS}$ in the range of relative pressure below 0.30, suggesting that $\text{SO}_3\text{H-Si-HS}$ (with a more hydrophilic surface character) could also adsorb higher amounts of acetone than $30 \text{ SO}_3\text{H-E-HS}$ (with a less hydrophilic surface character).

Based on the gas adsorption experiment, it can be concluded that the sulfonic acid-functionalized hollow nanospheres with hydrophilic surface properties favor high conversions and high selectivities for MIBK because of the preferred enrichment of acetone on the catalyst surface. Our studies show that tuning the surface properties of the catalytic materials is an efficient strategy to improve the catalytic performance of a solid catalyst according to the polarity of the reactant and product.

The catalytic performance of Pd/SO_3H -Si-HS, Pd/SO_3H -FDU-12, and Pd/SO_3H -SBA-15 was compared in one-pot syntheses of MIBK. These materials have different morphologies, but comparable acidities. Pd/SO_3H -Si-HS exhibited a much higher activity and selectivity for MIBK than Pd/SO_3H -FDU-12 and Pd/ SO_3H -SBA-15 (Table 2). This is probably due to the fact that the high ratio of the external surface area of the hollow nanospheres and thin shell thickness can increase the accessibility of the guest molecules to the active sites, reduce the diffusion resistance, and shorten the diffusion pathway of MIBK to avoid the deep condensation route.^[3c]

The effect of temperature was studied over the range of 100–180 $^\circ\text{C}$ (Table 4). As expected, the conversion of acetone increased monotonously with the increase in temperature. The

Table 4. Influence of temperature on the catalytic performance of Pd/ $30SO_3H\mbox{-}E\mbox{-}HS$ in the one-pot synthesis of MIBK. $^{[a]}$									
Temperature Conversion Selectivity [%] [°C] [%] MIBK DIBK C ₃ IP MO others									
100	9.7	74.2	0	2.1	18.7	0	5.0		
120	15.3	79.7	0.1	3.0	16.6	0.3	0.2		
140	25.0	84.4	3.5	3.0	7.8	0.3	1.0		
160	36.1	86.2	4.9	2.2	5.9	0.1	0.7		
180	49.8	82.7	6.4	4.0	4.6	0.3	2.0		
[a] Reaction conditions are the same as in Table 2 with the exception of reaction temperature.									

selectivity for MIBK reached the maximum value at 160 °C. IP was the major side product at temperatures below 140 °C, and the amount of DIBK increased in parallel with reaction temperature. This showed that the hydrogenation of acetone was the major side reaction at low temperatures and the over-condensation of MIBK with acetone was the main side reaction at high reaction temperatures.^[8] Through adjustment of the reaction conditions, the selectivity to MIBK could be increased from 74 to 86%.

A main advantage of heterogeneous catalysis is the easy recycling of catalysts and the facile separation of the products. We thus also tested the reuse ability of the solid catalyst Pd/ $30SO_3H$ -E-HS. The selectivity for MIBK regained its initial level, albeit with reduced conversion of acetone during the recycling process (Table 5). Pd/ $30SO_3H$ -E-HS still retained 62% of its original activity for the fifth cycle. Regeneration of the catalysts was accomplished by stirring Pd/ $30SO_3H$ -E-HS in dilute aqueous H₂SO₄. The activity of the regenerated catalyst returned to its original level, and the catalyst could be reused for another two cycles with conversions of acetone above 31%. That indicated that hollow nanospheres are robust catalysts with numerous potential applications.

Table 5. Recycling of Pd/30 $\rm SO_3H\mathchar`-HS$ in the one-pot synthesis of $\rm MIBK.^{\rm [a]}$										
Entry	Conversion [%]	Selectiv MIBK	vity [%] DIBK	C ₃	IP	МО	others			
1	36.1	86.2	4.9	2.2	5.9	0.1	0.5			
2	31.6	89.2	3.5	2.8	3.2	0	1.3			
3	29.9	91.3	1.8	1.8	3.3	0	1.8			
4	27.8	87.8	1.9	2.5	5.3	0	2.5			
5	22.4	86.2	3.1	3.1	4.9	0	2.7			
6(H ⁺) ^[b]	36.1	88.4	3.1	3.1	4.9	0	3.3			
7	34.0	86.2	5.3	3.2	2.7	0	2.6			
8	31.1	88.4	3.5	2.9	3.2	0	2.0			
[2] Reaction conditions are the same as in Table 2, 200 mg of catalyst										

used for all entries. [b] Pd/30 SO₃H-E-HS was regenerated after five cycles.

Conclusions

Sulfonic acid-functionalized hollow nanospheres with different surface properties were prepared by co-condensation of 1,2bis(trimethoxysilyl)ethane (BTME) or tetramethoxysilane (TMOS) with 3-mercaptopropyltrimethoxysilane (MPTMS) followed by postsynthesis oxidation. After doping with Pd, the sulfonic acid-functionalized hollow nanospheres were active and selective for the one-pot synthesis of MIBK from acetone. Hollow nanospheres with hydrophilic surface properties were more active and selective than those with hydrophobic surface properties, probably due to the enrichment of acetone by hydrophilic hollow nanospheres. Moreover, the catalyst with hollow nanospherical morphology exhibited higher activity than its bulk mesoporous counterparts, which was probably due to the fact that the unique hollow spherical morphology (with particle sizes on the nanoscale) enhances the accessibility of the active sites to the reactants and the fast diffusion of the reactant and products. We demonstrated the improvement of catalytic performance of the solid catalysts by tuning their surface properties and morphology.

Experimental Section

Chemicals

All materials were of analytical grade and used as received without any further purification. MPTMS was purchased from Gelest Inc. (Germany). Triblock copolymer $EO_{106}PO_{70}EO_{106}$ (F127), $EO_{70}PO_{20}EO_{70}$

(P123), BTME, DA, MO, and DIBK were purchased from Sigma–Aldrich. Amberlite 120 with a dry acidity of 4.4 mmol g⁻¹ was purchased from Alfa Aesar. The resins were heated under vacuum at 120 °C before use to remove adsorbed water. $PdCl_2$ with a Pd content of 59 wt% was used as the metal precursor. Other reagents were obtained from Shanghai Chemical Reagent Inc. (Chinese Medicine Group).

Syntheses

SO₃H-functionalized ethane-silica hollow nanospheres (nSO₃H-E-HS): The material was synthesized according to a modified method developed by us.^[9] In a typical synthesis, F127 (0.80 g) and sodium acetate (1.38 g, 16.80 mmol) were dissolved in deionized water (28 mL) at 20 °C under vigorous stirring. After dissolution of the copolymer, the mixture of BTME and MPTMS was added under stirring. The molar composition of the mixture was Si/F127/NaOAc/ H₂O = 100:0.63:168:15560. The resultant mixture was stirred at 20°C for 24 h and aged at 100°C under static conditions for 24 h. The solid product was recovered by filtration and air-dried at room temperature overnight. Finally, the surfactant was extracted by heating a solution of the as-synthesized material (1.0 g) in ethanol (200 mL) and concentrated aqueous HCl (1.5 g) at reflux for 24 h. After extraction of the surfactant, the resulting solid (1.0 g) was dispersed in H₂O₂ (30 wt% in aqueous solution, 40 g). The resultant mixture was stirred for 12 h at 25 °C. After filtration, the solid material was stirred in H₂SO₄ (200 mL, 0.1 M) for 12 h at room temperature for acidification. After thoroughly washing with deionized water, the solid product was dried at 60 °C overnight. The sample was denoted as nSO₃H-E-HS (ethylene group in the network), where n (n = 10, 20, 30, 40) was the mol% ratio of MPTMS/ (BTME+MPTMS) in the initial mixture. The acid exchange capacities of nSO₃H-E-HS were determined by acid-base titration.

 SO_3H -functionalized silica hollow nanospheres (SO_3H -Si-HS): The material was synthesized according to a modified method previously developed by us^[10] using a mixture of TMOS and MPTMS as the silane sources [the MPTMS/(TMOS+MPTMS) mol% ratio was 20%]. This sample was denoted as SO_3H -Si-HS (network composed of pure silica).

 SO_3H functionalized SBA-15 (SO_3H -SBA-15) and FDU-12 (SO_3H -FDU-12): The materials were synthesized according to a modified method previously developed by us^[11] using a mixture of tetraethyl orthosilicate (TEOS) and MPTMS as the silane sources [the MPTMS/ (TEOS+MPTMS) mol% ratio was 20%]. The samples had 2D meso-channels and a cage-like porous structure and were denoted as SO_3H -SBA-15 and SO_3H -FDU-12, respectively.

Immobilization of Pd onto SO_3H -functionalized materials: The Pddoped catalysts were prepared by impregnation. SO_3H -functionalized materials were mixed with an aqueous solution of $PdCl_2$ (0.02 M) acidified with a few drops of HCI (2.0 M), followed by solvent evaporation in a rotary evaporator and subsequent washing with water to remove residual H⁺ and Cl⁻ ions. The reduction of Pd^{II} to Pd⁰ was accomplished in a hydrogen flow (30 mL min⁻¹) at 200 °C for 2 h. The Pd-loaded $n SO_3H$ -E-HS, SO_3H -Si-HS, SO_3H -SBA-15, and SO_3H -FDU-12 were denoted as Pd/ $n SO_3H$ -E-HS, Pd/SO₃H-Si-HS, Pd/SO₃H-SBA-15, and Pd/SO₃H-FDU-12, respectively. Their content in Pd was 1.0 wt %.

General process for the one-pot synthesis of MIBK catalyzed by the solid catalyst: The one-pot synthesis of MIBK was carried out in a 20 mL stainless steel autoclave equipped with a pressure gauge and a magnetic stirrer. Typically, the autoclave was charged with

acetone (2.0 g), n-nonane (0.50 g, internal GC standard), and catalyst (0.20 g). Before reaction, the autoclave was purged three times with H₂, then pressurized with H₂ and placed in an oil bath, which was preheated to the reaction temperature, and was stirred with a speed of 800 rpm. Judging from the resulting pressure, most of the acetone remained liquid under such conditions. After reaction, the autoclave was cooled in an ice bath at 0°C, depressurized in a gas bag with a stopcock to collect gaseous products (propene and propane), and opened. The reaction mixture was then removed from the autoclave and the products were separated from the catalyst by centrifugation. The liquid products were identified by comparison with the standard substance and quantified by GC analysis, using an Agilent Technologies 6890 instrument equipped with a flame ionization detector and a 30 m×0.25 mm poly(ethylene glycol) (PEG) capillary column (Dalian Elite Co.). To recycle the solid catalyst, the catalyst was filtered from the reaction system, thoroughly washed with ethanol, dried for 5 h at 80 °C, and directly used in the next cycle. Regeneration of the catalysts was accomplished by stirring the used catalysts in aqueous H_2SO_4 (0.5 M).

Characterization

The nitrogen sorption experiments were performed at -196°C using a Micrometrics ASAP 2020 accelerated surface area and porosimetry analyzer. Samples were degassed at 120°C for 5 h prior to the measurements. BET specific surface areas were calculated using adsorption data at the relative pressure (P/P_0) range of 0.05-0.25. Pore-size distributions were derived from the adsorption branch by using the BJH method. The total pore volumes were estimated from the amounts adsorbed at $P/P_0 = 0.99$. TEM analyses were performed using a FEI Tecnai G2 Spirit transmission electron microscope at an acceleration voltage of 120 kV. Before examination, the samples were dispersed in anhydrous ethanol and deposited on a holey carbon film on a Cu grid. FTIR spectra were collected with a Nicolet Nexus 470 IR spectrometer (KBr pellets were prepared) in the range of 400-4000 cm⁻¹. Solid state diffuse reflectance UV/Vis spectra for powder samples were recorded by using a Shimadzu UV-2550 UV/Vis spectrophotometer equipped with an integrating sphere by using BaSO4 as a white standard. S elemental analyses were determined by means of an Elementar Vario EL III analyzer. CPMAS ¹³C (100.6 MHz) and MAS ²⁹Si NMR (79.5 MHz) experiments were recorded by using a Bruker DRX-400 spectrometer equipped with a magic-angle spin probe in a 4 mm ZrO₂ rotor using tetramethylsilane as reference. For CPMAS ¹³C NMR experiments the parameters used were: 8 kHz spin rate, 3 s pulse delay, 4 min contact time, and 1000 scans; for MAS ²⁹Si NMR experiments the parameters used were: 8 kHz spin rate, 3 s pulse delay, 10 min contact time, and 1000 scans. SEM was undertaken by using a FEI Quanta 200F scanning electron microscope operating at an accelerating voltage of 1-30 kV. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/Max-2500PC diffractometer with CuK_a radiation ($\lambda = 1.5418$ Å) over the 2 θ range of 5–70° with a scan speed of 5° min⁻¹ at room temperature. The adsorption of water and acetone vapors was measured at 20 °C on a Micrometrics ASAP 2020 instrument after the samples were degassed for 6 h at 80°C. The ultrapure water used in vapor adsorption experiments was produced by using a freeze-pump-thaw technology for three cycles. Acetone (AR grade) was first washed with a dilute KMnO₄ solution and then distilled with anhydrous Na₂SO₄, followed by three cycles of freeze-pump-thaw.

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