Electronic Supplementary Information for:

Amino-functionalized SBA-15 type mesoporous silica having nanostructured hexagonal platelet morphology

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Experimental

Synthesis method

For the direct synthesis of amino-functionalized SBA-15, a Pluronic P123 triblock copolymer (EO20PO70EO20, MW. 5800) was used as a structure-directing agent, a sodium metasilicate (Na2SiO3.9H2O) was used as a silica source and a 3-aminopropyl triethoxysilane/APTES (NH2(CH2)3Si(OEt)3) was used as an aminopropyl group source. The preparation of the initial synthesis mixtures were carried out according to the following procedures, 16 g of 10% (w/w) aqueous solutions of P123 were poured into 26.6 g distilled water and then 0.016-x moles of sodium metasilicate were added to the reaction mixtures followed by x moles of APTES (x = 3, 5, 7.5, and 10 to obtain NH2 to SiO2 molar ratios = 3, 5, 7.5, and 10% respectively). The mixtures were vigorously stirred by using mechanical stirrers at room temperature until homogenous solutions were obtained. To the vigorously stirred solutions, 13 g of concentrated hydrochloric acid (37.6%) was quickly added. The final mixtures were stirred for 1 hour at 313 K before subjected to the microwave digestion system (CEM Corporation, MARS-5). The microwave condition for crystallization was set under a static condition at 373 K for 2 h with operating power of 300 W (100%). The crystallized products were filtered, washed with warm distilled water and ethanol and finally dried at 333 K. The surfactant was then
removed by Soxhlet extraction over ethanol for 24 h. The obtained samples were noted as NH$_2$pr(x)-SBA-15 which x was the NH$_2$ to SiO$_2$ molar ratio in the initial reaction mixture. For example NH$_2$pr(7.5)-SBA-15 stand for the NH$_2$pr-SBA-15 synthesized with NH$_2$ to SiO$_2$ molar ratio = 7.5% in the initial reaction mixture.

Characterization

Mesostructures of the synthesized materials were identified by powder X-ray diffractions. The XRD patterns were obtained by using a Rigaku Multiflex diffractometer with a monochromated high-intensity Cu Ka radiation ($\lambda = 1.54$ Å). Scanning was performed under ambient conditions over the 2$\theta$ region of 0.6-4.5° at the rate of 0.1°/min (20 kV, 10 mA). The NH$_2$pr(5)-SBA-15 and NH$_2$pr(7.5)-SBA-15 showed very intense diffraction peaks at 2$\theta$ = 0.81 to 0.89° with four well-resolved peaks at higher degree which were characteristic for long range ordered SBA mesoporous materials family with a 2-D hexagonal symmetry (p6mm). The XRD main peak intensity of NH$_2$pr(10)-SBA-15 was weaker and only for 110 and 200 diffraction peaks were well-resolved at the higher degree.

The N$_2$ adsorption–desorption isotherms and pore characterization were obtained by using a Micromeritics ASAP 2020 apparatus at liquid N$_2$ temperature. Pore distributions were calculated by using BJH method from the adsorption branches.

For the observation of the synthesized NH$_2$pr(x)-SBA-15 by TEM, 1 mg of the materials was dispersed in 50 mL of ethanol and a drop of suspension was then spread on a holey amorphous carbon film deposited on Ni grid (JEOL Ltd.). The prepared samples were then examined in a high-resolution transmission electron microscopy (HR-TEM; JEOL JEM-2010). For all of the samples, the images of honeycomb pores arrangement typical for a 2D hexagonal mesoporous material were obtained. Furthermore, TEM specimen stage was tilted more than 30 degree continuously from the condition of honeycomb image to the other and 1D lattice images could be observed in the tilting. Channel direction of the 2D-hexagonal structures is parallel to the thickness direction of the nanostructured hexagonal platelet morphologies. And the scanning electron microscopic (SEM) images were collected with a JEOL 630-F microscope. Before the
measurement, the samples were dispersed onto a steel plate surface and coated with Pt metal.

The near infrared (NIR) diffuse reflectance spectra (DRS) were measured with a Solidspec 3700 UV-Vis-NIR spectrometer. For analysis, 200 mg of sample was loaded into a homemade quartz cell with 1 cm path length and evacuated under vacuum at 423 K. The NIR spectra were recorded in the reflectance mode at room temperature. A BaSO₄ was used for background. The presence of aminopropyl groups was confirmed by reflection bands at 1529 and 2020 nm which were assigned to the combination (ν\text{asym} + ν\text{sym}) band of asymmetry stretching (ν\text{asym}) and symmetry stretching (ν\text{sym}) modes and the combination (ν+δ) band of stretching vibration (ν) and bending (δ) modes of the primary amine groups, respectively. The reflection bands at 1630-1860 nm were assigned to the first overtone bands of CH₂ moiety stretching vibrations. It was observed that those bands intensities were increased with the increased of APTES amount added into the synthesis mixtures. This implies a higher loading of aminopropyl groups.

The CP MAS $^{13}$C solid state NMR spectrum was recorded on a Varian Unity-Inova 400. The experiment was carried out at 100 MHz with a 7 mm CP/MAS probe. The magic spinning frequency was set to 5 kHz. Elemental analyses were performed with EA-1110 (CE Instruments).

**Benazaldehyde and tert-butyl salicylaldehyde adsorption and Knoevenagal condensation.**

The accessibility and the state of the aminopropyl group in NH$_2$pr(7.5)-SBA-15 material was investigated by using the condensation reactions of the amino group with benaldehyde and tert-butyl salicylaldehyde to give imines. In the typical reaction, 200 mg of the catalyst was treated with 2 mmol benzaldehyde or tert-butyl salicylaldehyde in anhydrous toluene under constant stirring at room temperature for 12 h. The catalyst was filtered and washed with toluene to eliminate the unreacted reactants. The filtrate including the excess reactant was analyzed by gas chromatography with dodecane as a internal standard.

Before being used in catalytic reaction, the extracted catalyst (1 g) was neutralized with 100 ml of 0.2 M tetramethylammonium hydroxide (TMAOH) solution in
methanol under constant stirring for 30 min. The catalyst was recovered by filtration and washed several times with methanol. The catalyst was dried and evacuated under vacuum at 433 K for 12 h.

The catalytic activities of NH₂pr(7.5)-SBA-15 for Knoevenagal condensation between benzaldehyde and ethyl cyanoacetate were investigated at 303 K with toluene as solvent. In typical catalytic reaction, a mixture of 50 mg catalyst, $x$ mmol benzaldehyde, $x$ mmol ethyl cyanoacetate (with $x = 1.5; 3$; and $6$) and 1 ml toluene was introduced into the reaction vessel and heated at 303 K with constant stirring. Small amount of reaction mixture was frequently removed from the reaction vessels and subsequently the reaction products were analyzed by gas chromatography with dodecane as an internal standard.
S1. N$_2$ adsorption-desorption full isotherms of NH$_2$pr(x)-SBA-15 with different NH$_2$ to SiO$_2$ molar ratio in the initial synthesis mixtures. The sharp steep increases in the adsorption isotherms were observed at P/Po: (a) 0.8 for NH$_2$pr(5)-SBA-15; (b) 0.77 for NH$_2$pr(7.5)-SBA-15; and (c) 0.71 for NH$_2$pr(10)-SBA-15.
S2. Pore distributions of NH$_2$pr(x)-SBA-15 calculated by using BJH method from the adsorption branches.
S3. SEM and TEM images of NH₂pr-SBA-15 synthesized from a reaction gel with NH₂ to SiO₂ molar ratio 3%.
S4. TEM images of (a) NH$_2$pr(5)-SBA-15; (b) NH$_2$pr(7.5)-SBA-15; and (c) NH$_2$pr(10)-SBA-15. For all of the samples, the images of honeycomb pores arrangement typical for a 2D hexagonal mesoporous materials were obtained with the channel direction of the 2D-hexagonal structures parallel to the thickness direction of the nanostructured hexagonal platelet morphologies.
S5. Near infrared (NIR) spectra of NH$_2$pr(x)-SBA-15 synthesized with different NH$_2$ to SiO$_2$ molar ratio in the initial synthesis mixtures.
S6. $^{13}$C CP MAS NMR spectrum for NH$_2$pr(7.5)-SBA-15

S7. Physicochemical properties of NH$_2$pr(x)-SBA-15 with different NH$_2$ to SiO$_2$ molar ratio in the initial synthesis mixtures.

<table>
<thead>
<tr>
<th>Sample NH$_2$pr(x)-SBA-15</th>
<th>N content (mmol/g)$^a$</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore size (nm) from adsorption branch</th>
<th>Pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
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<td>680</td>
<td>9.0</td>
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$^a$ Calculated from CHNS elemental analysis results