

## Basic Functionalization of Hexagonal Mesoporous Silica

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**Abstract:** 3-Aminopropyltriethoxysilane (AM), 3-ethyldiaminopropyltrimethoxysilane (ED) and 3-piperazinylpropyltriethoxysilane (PZ), were used to chemically couple with the silanol groups of calcined hexagonal and hexagonal-like mesoporous silica SBA-3 and HMS, respectively, to produce functionalised alkaline mesoporous materials. The increase in the dosage of organosilanes, or in reaction temperature, or in the humidity (*i.e.*, water content) of support, is favorable to the grafting of functional molecules on the surface. When functionalization conditions are the same, the order of loadings on SBA-3 and DDA-HMS is ED>AM>PZ. However, on ODA-HMS, the loading of AM is similar to that of ED.

**Keywords:** Hexagonal mesoporous silica, surface functionalization, organosilanes.

Recently, a novel method of modification, *i.e.*, functionalizing the internal surface of mesoporous materials has been reported<sup>1-5</sup>, owing to the large pore size, the silanol groups, which are in a big population in mesoporous materials, can chemically couple with the active groups of some bulky organic functional molecules. Based on this approach, one can obtain novel solid basic catalysts. Here we functionalized the hexagonal and hexagonal-like mesoporous silica materials SBA-3 and HMS with three organosilanes, 3-aminopropyltriethoxysilane (AM), 3-ethyldiaminopropyltrimethoxysilane (ED) and 3-piperazinylpropyltriethoxysilane (PZ), and investigate for the first time the effects of functionalization conditions, such as the dosage of organosilane, the humidity (*i.e.*, water content) of mother sample and so on, on the loadings and the bonding degree of functional molecules.

### Experimental

The SBA-3 was synthesized as previously described<sup>6</sup>. The DDA-HMS and ODA-HMS samples were prepared in the acidic media (pH=2) at the composition ratio: 1TEOS : 0.27DDO(ODA): 6.5EtOH : 36H<sub>2</sub>O. The as-synthesized samples were calcined to remove templates at 550°C. In order to investigate the influence of humidity (*i.e.*, water content) of mother samples on functionalization, the calcined samples were not evacuated

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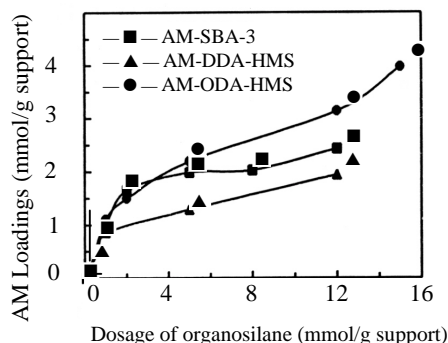
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or further evacuated (20 Pa for 0.5 h at 150°C) for a given time to remove the adsorbed H<sub>2</sub>O in air, before they were functionalized. For comparison, a part of calcined samples were set in a desiccator containing saturated NaCl solution for hydration for a given time and then were functionalized. The functionalization were conducted by mixing the samples with given organosilane in toluene, followed by stirring for 3 h or longer time at given temperature. The treated samples were filtered and the extra organosilane were extracted with CH<sub>2</sub>Cl<sub>2</sub> twice. The obtained samples were designated as AM (or ED, PZ)-SBA-3 (or DDA-HMS, ODA-HMS). N<sub>2</sub> adsorption measurements were performed on Micromeritics ASAP 2000 instrument after evacuation at 300°C and 5×10<sup>-3</sup> mmHg. The C, N element analysis are conducted on Perkin-Elmer 2000 instrument.

### Results and Discussion

As shown in **Figure 1**, the amount of organosilanes influenced the functionalization level as expected. When the dosage of organosilane increased from 0 to 2 mmol/g support, the loading (mmol/g support) increased rapidly, and then increased slowly upon the further increase in dosage of organosilane. The loading also increased with the increase of temperature (**Figure 2**). When the temperature increased from 80°C to 120°C, the loading of AM on SBA-3 increased about 10%. However, elongating reaction time did not influenced the loading obviously (not shown here). Besides the dosage of organosilane, the humidity (*i.e.*, water content) of mother samples are another factors which influence the functionalization level significantly. As shown in **Table 1**, the loading amount of AM over SBA-3 obeyed the sequence: Hydration > no activation > activation. The loading of AM over SBA-3 sample without further activation increased by over 30% in comparison with that for the SBA sample activated for 5 h. However, although the loading increased, the excessive humidity of samples destabilized the sample, and no catalytic activation was observed, that means the increased loading was mainly caused by the condensation between the organosilane molecules, a detailed explanation will be given in our full paper in preparation.

**Figure 1** Effect of dosage of organosilane on loading of AM.



Conditions for functionalization reaction: 120°C for 3 h, no activation pre-treatment on mother samples.

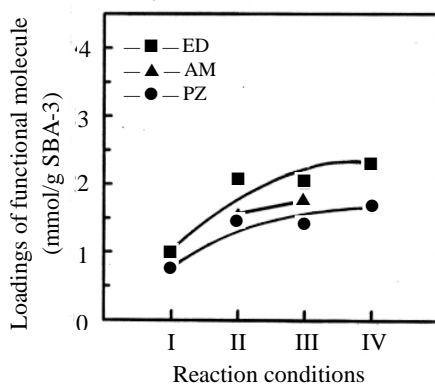
**Table 1** Effect of humidity of mother sample on functionalization

Sample	Pretreatment <sup>a</sup>	Dosage <sup>b</sup> (mmol/gSBA-3)	C/N	Org-content <sup>c</sup> (%)	Loading <sup>d</sup> (mmol/gSBA-3)
AM-SBA-3-1	Hydration for 2 h	12	3.44	27.9	4.04
AM-SBA-3-2	No activation	12	3.77	20.0	2.43
AM-SBA-3-3	Activation for 5 h	12	4.82	18.2	1.76
AM-SBA-3-4	No activation	5	4.09	18.0	1.99
AM-SBA-3-5	Activation for 5 h	5	4.49	17.5	1.77
AM-SBA-3-6	Activation for 10 h	5	4.51	16.7	1.68

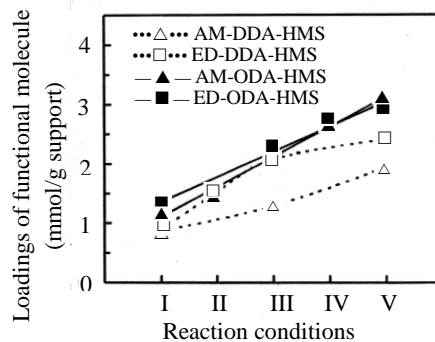
Conditions for functionalization reaction: 120°C for 3 h.

a. Pretreatment conditions for mother samples; b. Dosage of organosilane;

c. Content of organic component in functionalised sample; d. Loading of functional molecule.

**Figure 2** Loadings of different molecules functional groups on SBA-3 activated at 150°C, 20 Pa, 5 h.

(I) r.t. for 3 h, 1 mmol/g; (II) 80°C, 3 h, 5 mmol/g; (III) 120°C, 3h, 5 mmol/g; (IV) 120°C, 3 h, 12 mmol/g.

**Figure 3** Loadings of different molecules functional groups on not activated DDA-HMS (dotted line) and ODA-HMS (solid line), 120°C, 3 h.

Furthermore, as shown in **Figure 2** and **3**, the loading was influenced by both the pore size of mesoporous materials and the size of organosilanes. For the SBA (diameter of pore size=2.12 nm), and DDA-HMS (diameter of pore size=2.35 nm) samples, the loading level sequence was: ED>AM>PZ. This should be caused by the greatest size of PZ and the smallest size of AM. However, when the loading was performed over ODA-HMS (diameter of pore size=3.04 nm), not only the loadings increased, but also the difference between the loadings for AM and ED became much smaller than those over SBA and DDA-HMS. This is suggested that the bigger pore size of ODA-HMS allowed the entrance of more AM molecules. All of the above results will be discussed in detail elsewhere.

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