

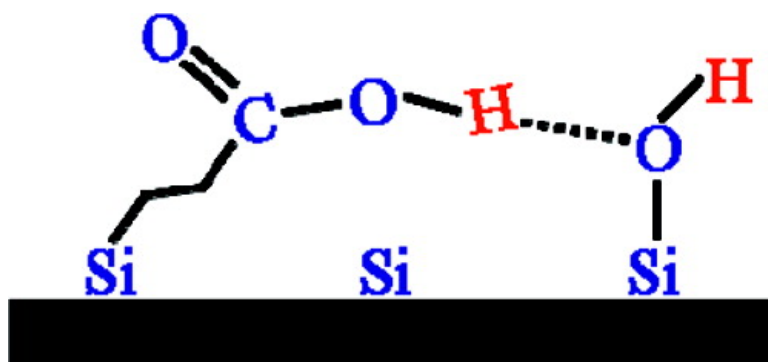
Communication

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## Direct Evidence for Interactions between Acidic Functional Groups and Silanols in Cubic Mesoporous Organosilicas

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Since the discovery of the ordered M41S family of mesoporous materials, functionalization of mesoporous materials via organic modifications has received considerable attention.<sup>1</sup> The presence of organic groups with many favorable properties allows the surface properties of these mesoporous silica materials to be tuned for various practical applications such as catalysis, separation, and adsorption of heavy metals. To produce mesoporous materials with relatively uniform distribution and high loadings of the organic functionalities, a so-called direct synthesis method involving the co-condensation of organotrialkoxysilane with another silica source, such as tetraethoxysilane (TEOS), has been developed. For example, SBA-15, HMS, and MCM-41 mesostructures have been functionalized with sulfonic acid groups using the direct synthesis approach.<sup>2</sup> Corriu et al. reported an ordered SBA-15 containing phosphonic acid groups by the same synthetic method.<sup>3</sup>

Carboxylic acid is a well-known reactive group and a good ligand for chemical species and possesses the ability to form hydrogen bonds. However, relatively few studies have focused on the preparation of mesoporous materials functionalized with carboxylic acid (–COOH) groups. The preparation of mesoporous materials functionalized with the –COOH groups generally involves two steps: the synthesis of cyanide-modified parent silica and subsequent hydrolysis of cyanide groups to carboxylic groups using H<sub>2</sub>SO<sub>4</sub> as catalyst,<sup>1b,c,4</sup> based on the fact that the –CN groups are reactive to water under acidic conditions. A mesoporous silica film with a –COOH-terminated pore surface has also been reported.<sup>5</sup> Yang et al. showed that the direct-synthesized cyanide-functionalized SBA-15 can be further treated with sulfuric acid to remove the template and carboxylate-functionalized SBA-15 can be simultaneously formed.<sup>6</sup>

Recently, the cage-like mesoporous materials such as SBA-1 have received considerable attention because of their fascinating 3D mesoporous structures.<sup>7</sup> However, little research has been reported on the direct synthesis of organo-functionalized SBA-1 due to the poor stability of the as-synthesized SBA-1 toward washing with water.<sup>8</sup> We have recently reported that incorporation of thiol groups can improve the inherent poor stability of the SBA-1 mesostructure.<sup>9</sup>

One of the major interests of mesoporous organosilicas is the framework location of organic functional groups. Mesoporous silicas functionalized with thiol groups are often represented in the form of organic branched spatially arranged along the pore channel in a configuration perpendicular to the silica walls with thiol groups pointing at the center of the mesopore.<sup>10</sup> Such a schematic view appears to be adequate since no interaction between thiol functional and silanol groups is expected to occur. It would be less appropriate if the incorporated organic functional groups interact strongly with silanol groups. However, direct spectral evidence for the interactions between the organic functional and silanol groups in mesoporous organosilicas is often not achievable. Since carboxylic acid possesses the ability to form hydrogen bonds, mesoporous silicas functionalized with carboxylic acid groups would be good candi-

dates for probing the interactions between the organic functional and silanol groups.

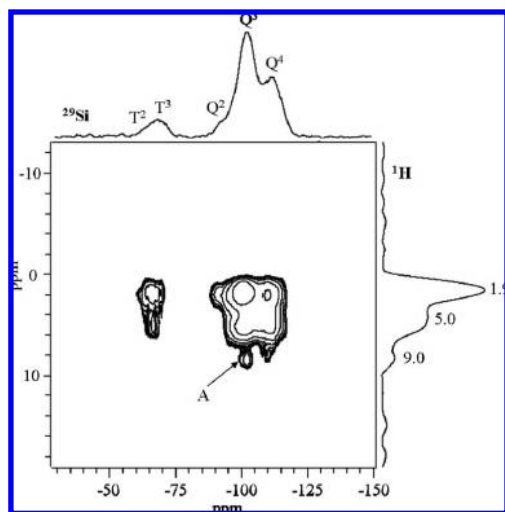
Here we report a facile synthesis route for preparation of SBA-1 functionalized with carboxylic acid groups. It involves a one-pot synthesis using tetramethoxysilane (TMOS) and 2-cyanoethyltriethoxysilane (CNTESE), with a molar ratio of 5:1, as silicon sources templated by cetyltriethylammonium bromide (CTEABr) under acidic conditions of H<sub>2</sub>SO<sub>4</sub>.<sup>10</sup> To the best of our knowledge, no direct synthesis of –COOH-functionalized SBA-1 has yet been reported.

The structural properties of the –COOH-functionalized SBA-1 material were characterized by using X-ray diffraction (XRD) and N<sub>2</sub> sorption measurements (Figure S1, Supporting Information (SI)). The powder XRD pattern of the template-extracted sample showed three well-resolved XRD diffraction peaks in the region  $2\theta = 1.5^\circ - 2.5^\circ$ , which can be indexed to the (200), (210), and (211) diffractions, characteristic of the cubic *Pm3n* mesostructure. The nitrogen adsorption–desorption isotherm indicated that the material exhibited a high surface area of 1065 cm<sup>2</sup>/g, a pore volume of 0.74 cm<sup>3</sup>/g, and a pore size of 2.8 nm. The TEM image also showed that the material exhibited a highly ordered structure (Figure S2, SI). All of these characteristics are indicative of a well-ordered SBA-1 silica framework with a uniform porosity.

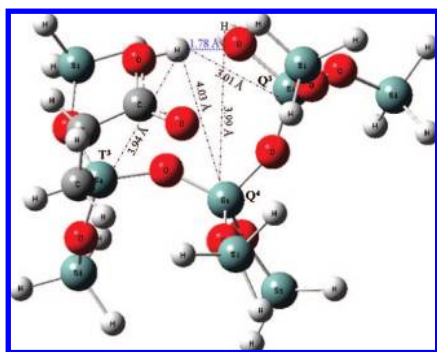
The successful incorporation of the functional groups into the silica framework was identified by <sup>29</sup>Si magic angle spinning (MAS) NMR. Five signals at –92, –101, and –110 ppm, corresponding to Q<sup>2</sup> (Si(OSi)<sub>2</sub>(OH)<sub>2</sub>), Q<sup>3</sup> (Si(OSi)<sub>3</sub>(OH)), and Q<sup>4</sup> (Si(OSi)<sub>4</sub>) species, and at around –66 and –55 ppm, corresponding to T<sup>3</sup> (RSi(OSi)<sub>3</sub>, where R refers to the cyanoethyl group) and T<sup>2</sup> (RSi(OSi)<sub>2</sub>(OH)) species, were observed (Figure S3, SI). A T<sup>m</sup>/(T<sup>m</sup> + Q<sup>n</sup>) ratio of 0.16 is in close agreement with the composition in the initial reaction mixture.

<sup>13</sup>C cross polarization magic angle spinning (CPMAS) NMR not only confirms the presence of organic functional groups but also serves as a powerful tool to determine the conditions at which the –CN groups undergo transformation. The peak at 177 ppm due to the carboxylate groups, associated with two peaks at 28 and 8 ppm due to the ethyl groups, was dominated while the peak at 120 ppm expected for the –CN group was not observed (Figure S3, SI). This finding indicated that –CN groups have completely been hydrolyzed to –COOH groups under such acidic conditions.

2D <sup>29</sup>Si{<sup>1</sup>H} HETCOR (heteronuclear correlation) NMR was further employed to examine the framework location of the carboxylic acid groups within SBA-1 after template removal (Figure 1). It is advantageous for such an HETCOR NMR experiment to measure only correlations between spatially adjacent silicon species. The <sup>1</sup>H peak at 1.9 ppm from Si–OH groups is predominantly correlated to the Q<sup>3</sup> species and to both T and Q<sup>4</sup> species as well. The methylene protons in T species also make a contribution to the <sup>1</sup>H signal at 1.9 ppm. All these species also have correlations with the peak at 5.0 ppm due to the residual water molecules in



**Figure 1.**  $^{29}\text{Si}\{^1\text{H}\}$  2D HETCOR NMR spectrum of carboxylic acid functionalized SBA-1 after template removal, acquired with a contact time of 3 ms and at a spinning speed of 5 kHz.



**Figure 2.** Optimized structure of the  $\text{T}^3\text{-Q}^4\text{-Q}^3$  motif with one hydrogen bond between  $\text{T}^3$  and  $\text{Q}^3$  obtained from density functional theory calculations.

the sample. The T species do not show any correlation to the peak at 9.0 ppm, which is attributed to the carboxylic proton ( $-\text{COOH}$ ). This is reasonable since the Si atom in the T species is distant from the carboxylic protons. Notably, the peak at 9.0 ppm is clearly correlated to the  $\text{Q}^3$  species (correlation peak A in the figure) as compared to the  $\text{Q}^4$  species. This observation suggests a preferable distribution of the  $-\text{COOH}$  functional groups; that is, the  $\text{T}^3$   $-\text{COOH}$  groups are in closer proximity to the  $\text{Q}^3$  species than to the  $\text{Q}^4$  species. The present NMR result provides direct evidence for the presence of a specific interaction, e.g., hydrogen bonding, between the  $\text{T}^3$   $-\text{COOH}$  groups and the  $\text{Q}^3$  Si-OH groups.

Since carboxylic acid possesses the ability to form hydrogen bonds, density functional theory calculations within the suite of Gaussian 03 programs<sup>11</sup> were performed on two major framework compositions, i.e., the  $\text{T}^3\text{-Q}^3\text{-Q}^4$  and  $\text{T}^3\text{-Q}^4\text{-Q}^3$  motifs, to explore the possible hydrogen bonding between the various Si units using the calculated  $^1\text{H}$  chemical shifts of the free  $\text{T}^3$   $-\text{COOH}$  (5.97 ppm) and  $\text{Q}^3$  Si-OH (1.36 ppm) monomers as the references. The optimized structure of the  $\text{T}^3\text{-Q}^4\text{-Q}^3$  motif (Figure 2) shows that the polar hydrogen of the  $\text{T}^3$   $-\text{COOH}$  group forms one hydrogen bond with the oxygen of the  $\text{Q}^3$   $-\text{OH}$  group. The calculated  $^1\text{H}$  chemical shifts of  $\text{T}^3$   $-\text{COOH}$  and  $\text{Q}^3$  Si-OH groups are 10.39

and 1.91 ppm, respectively. This hydrogen bonding interaction results in a short H-Si distance (3.01 Å) between the  $\text{T}^3$  carboxylic proton and the  $\text{Q}^3$  Si atom and a long H-Si distance (3.94 Å) in  $\text{T}^3$ . Both the structural characteristics and calculated NMR shifts in the  $\text{T}^3\text{-Q}^4\text{-Q}^3$  motif are in good agreement with the observations of  $^{29}\text{Si}\{^1\text{H}\}$  HETCOR NMR experiments. The presence of the  $\text{T}^3\text{-Q}^4\text{-Q}^3$  motif with two hydrogen bonds (Figure S4, SI) cannot be excluded since its calculated  $^1\text{H}$  chemical shift of  $\text{Q}^3$  Si-OH (6.05 ppm) may contribute to the observed  $^1\text{H}$  signal at 5.0 ppm (Figure 1). On the other hand, the structural features of the  $\text{T}^3\text{-Q}^3\text{-Q}^4$  motif did not fit in the NMR experimental observations (Figure S5 and Table S1, SI). The combined results of  $^{29}\text{Si}\{^1\text{H}\}$  HETCOR NMR and density functional theory calculations indicate that the  $\text{T}^3\text{-Q}^4\text{-Q}^3$  motif is the favorable framework composition in carboxylic acid functionalized cubic mesoporous silica SBA-1. This is of great importance because the framework location and distribution of the organic functional groups in mesoporous organosilicas is better understood.

In conclusion, we have demonstrated a facile one-pot synthesis route for preparation of a well-ordered cubic mesoporous silica SBA-1 functionalized with  $-\text{COOH}$  functional groups. The transformation of  $-\text{CN}$  groups into  $-\text{COOH}$  groups can be achieved simply by using  $\text{H}_2\text{SO}_4$  as the acidic medium. The utility of two-dimensional solid-state NMR techniques, in combination with theoretical calculations, to provide a deeper insight into the framework location of the acidic functional groups in mesoporous organosilicas can be visualized.

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**Supporting Information Available:** Complete ref 11 and texts for synthesis and characterization of carboxylic acid-functionalized SBA-1. XRD pattern,  $\text{N}_2$  sorption isotherm, TEM, and solid-state NMR spectra (Figures S1–S3). Theoretical calculation models and results for the  $\text{T}^3\text{-Q}^4\text{-Q}^3$  with two H-bonds and  $\text{T}^3\text{-Q}^3\text{-Q}^4$  motifs (Figures S4 and S5, Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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