

## Chloropropyl-modified MCM-41 as Gas Chromatography Matrix for the Separation of Water–Alcohol Mixtures

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In the present work, chloropropyl-functionized MCM-41 were prepared by a simple synthetic pathway and firstly studied as gas chromatography matrix for the separation of water–alcohol mixtures.

Mesoporous materials, such as those of the M41S class (especially MCM-41,<sup>1</sup> pillared clays and analogues), have attracted much attention due to their high surface areas, extremely narrow pore size distribution, and perfectly adjustable pore size. They have exhibited new perspectives in the fields of catalysis, separation, and adsorbents. Recently, much interest has been focused on applications in the area of separation, for example as chromatography stationary phases.<sup>2</sup> In 1994, Stefais et al. found that pillared clays with micro/mesoporous could separate inert gas mixtures and hydrocarbons,<sup>3</sup> suggesting the possibility of using M41S solids in chromatographic separation, and in particular as stationary phases for gas–solid chromatography. MCM-41 materials were first used as models for testing one-dimensional pore structure theories applied to size-exclusion chromatography.<sup>4</sup> MCM-41 silicas were also proposed as possible stationary phases for normal-phase HPLC,<sup>5</sup> reversed-phase HPLC,<sup>6</sup> capillary gas chromatography,<sup>7</sup> and enantioselective HPLC.<sup>8</sup> Raimondo et al.<sup>7</sup> have found that it is possible to coat GC capillary columns with mesoporous silica-based MCM-41 for separating organic molecules. Recently, Galarneau et al. have found that the ordered porosity enhances superior chromatographic performance to class silica-based columns by providing higher and more homogeneous molecular diffusivity.<sup>6</sup> A great deal of research showed that the mesoporous MCM-41 was a good candidate for the possible stationary phases due to high surface area, which is a great advantage to enhance the thermodynamic behavior of the classical stationary phase. However, up to now, there have been few reports on the use of MCM-41 as stationary phases for the separation of water–alcohol mixtures though the separation of water–alcohol mixtures is a very important and challenging problem due to their tendency to form the azeotropes.<sup>9</sup>

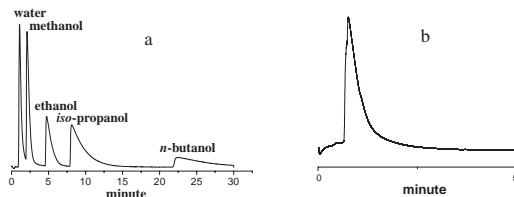
In the present work, chloropropyl-functionized MCM-41 were prepared by a simple synthetic pathway and studied as gas chromatography matrix for the separation of water–alcohol mixtures. Chloropropyl-functionized MCM-41 were prepared by a direct co-condensation synthesis,<sup>10</sup> cetyltrimethylammonium bromide (CTAB) as surfactant, chloropropyltrimethoxysilane (CPTMS) as modifiers. The molar ratio of reagents was: 1TEOS:0.29CPTMS:0.25CTAB:0.3NaOH:75H<sub>2</sub>O. The surfactant molecules were removed by ion-exchange procedure by treating as-made compounds with an ethanolic solution of ammonium nitrate at 333 K. For comparison, hybrid silica gel

was also prepared from the same raw materials as those used for preparation of the MCM-41 except for the addition of the template. The mesoporous nature of the material was confirmed by X-ray diffraction (XRD), high-resolution transmission electron microscope (HRTEM) and N<sub>2</sub> adsorption/desorption (See Supporting Information). Their stability was determined by thermogravimetric analysis (TGA) (See Supporting Information). The results of XRD and HRTEM indicated that the obtained materials were typical ordered hybrid mesophases. N<sub>2</sub> adsorption/desorption showed high surface areas (615 m<sup>2</sup> g<sup>-1</sup>) and narrow pore-size distribution. TGA revealed that the amount of chloropropyl group on the supports is 15% and the functionalized materials were found to be thermally stable up to 200 °C, indicating the strong chemical bond between chloropropyl group and MCM-41.

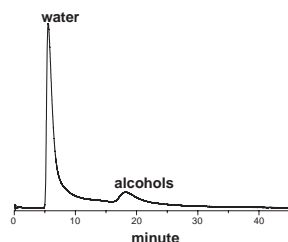
In a typical column preparation, a stainless steel pump (1-m long, 3-mm id) was filled with 0.9 g of functionalized MCM-41 (particle diameter of 0.15–0.18 mm). And then the packed column was aged for 24 h at 200 °C. The separation performance of the samples was investigated on the GC-950 (TCD). All the separation experiments were carried out under the conditions: *T* = 140 °C; *P*<sub>H<sub>2</sub></sub> = 0.2 MPa.

Figure 1 illustrates a typical separation of water–alcohol mixtures (1:1:1:1) with different matrix as stationary phase. It is clear that chloropropyl-modified MCM-41 exhibited good resolution and high efficiency for the tested water–alcohol mixtures (Figure 1a). In contrast, hybrid silica gel prepared from the same raw materials as those used for preparation of the MCM-41 showed no separation effect (Figure 1b). Considering that the walls of MCM-41 and silica gel are all made of amorphous silica, such a great difference between the separation effect may be attributed to the ordered porosity of the supports.

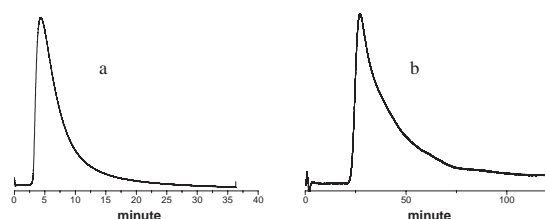
Nextly, the chloropropyl-functionalized MCM-41 samples were also prepared by grafting routes<sup>10</sup> and studied as matrix for the separation of water–alcohol mixtures. As shown in Figure 2, the grafted MCM-41 samples exhibit only two peaks



**Figure 1.** Gas chromatographic separation of water–alcohol mixtures using different matrix as stationary phase: (a) chloropropyl-modified MCM-41 and (b) chloropropyl-modified hybrid silica gel.



**Figure 2.** Gas chromatographic separation of water–alcohol mixtures using chloropropyl-modified MCM-41 matrix prepared by post synthesis grafting process as stationary phase.



**Figure 3.** Gas chromatographic separation of water–alcohol mixtures using different matrix as stationary phase: (a) aminopropyl-modified MCM-41 and (b) methyl-modified MCM-41.

and the alcohol mixtures are difficult to separate. Myong et al.<sup>10</sup> compared the synthesis of vinyl-functionalized MCM-41 samples by a post synthesis grafting process and a direct co-condensation synthesis. They found that the vinyl groups appeared to be more uniformly distributed throughout the channel surfaces by the latter than the before. Our Si NMR results (See Supporting Information) illustrate that the Si NMR spectrum of the chloropropyl-modified MCM-41 prepared by post synthesis grafting process showed two additional resonances that were assigned to R–Si(OH)<sub>2</sub>(OSi) (T<sup>1</sup>) and R–Si(OH)(OSi)<sub>2</sub> (T<sup>2</sup>), respectively. However the Si NMR spectrum of the chloropropyl-modified MCM-41 prepared by a direct co-condensation synthesis showed only T<sup>3</sup> and T<sup>2</sup> resonances, which suggested that chloropropyl groups were more tightly incorporated in the wall surfaces. Therefore, such a different separate efficient between the directed and post-grafted samples may be due to the distribution of the grafted chloropropyl group in the supports.

The effect of the groups grafted onto supports on the separation was investigated as shown in Figure 3. Surprisingly, when the hydrophilic MCM-41 functionalized with aminopropyl group and the hydrophobic MCM-41 with methyl group were used as supports instead of chloropropyl-modified MCM-41, no separation was observed, indicating that too much hydrophobic or hydrophilic surface is not required for the separation of water–alcohol system. Thus, it can be concluded that it is necessary to reach an equilibrium of the hydrophobic/hydrophilic ability on the surface for the efficient separation of the water–alcohol mixtures. The silica-based MCM-41 stationary phases have polar silanol groups on the surface, and the adsorption characteristics of MCM-41 for polar molecules such as water–alcohol system, greatly depend on the concentrations of surface silanol groups. In the present system, the chloropropyl groups are

anchored to inactivate the remaining silanol groups, so the much less polar chloropropyl silica surface shows only marginal retention of water and more significant retention of alcohols. The elution order is the most polar compound eluted first and the least polar species being the last eluted. On the other hand, the chloropropyl groups can interact with water and alcohol molecules by repulsive force and dispersive force within the confined room, where the longer the chain of the molecules is, the stronger the the repulsive force and the dispersive force are, that may make the interaction of the alcohol molecules with the supports are stronger than the water molecules. Also, water molecules have smaller molecular length and cross section area than that of other alcohols. Therefore, the desorption of water molecules should be faster than that of other alcohols within the confined room.

In conclusion, the first utilization of MCM-41 materials as supports for the separation of water–alcohol mixtures is reported. The chloropropyl-modified MCM-41 prepared by a direct co-condensation synthesis showed good resolution and high efficiency for the tested system. The ordered porosity of the supports, the distribution and capacity of the grafted chloropropyl group play an important role in the chromatographic separation of water–alcohol mixtures. Our results strongly suggest that the present chloropropyl-modified MCM-41 is very promising for gas chromatographic separation of water–alcohol mixtures. Also, it is believed that the high pure alcohol can be obtained from the water–alcohol mixtures.

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