Tailoring the Hydrophobicity of Mesoporous Organosilica for Protein Trapping and Supported Catalysis.

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I. Introduction

Molecular trapping and supported catalysis are applications of mesoporous materials with great industrial and scientific impact. A key parameter for their efficiency is the hydrophobicity of the surface, accompanied by a large surface area and the appropriate pore size3. Classic examples for applications in molecular trapping are the encapsulation followed by controlled drug delivery in nanomedicine5, the effective removal of the low concentrations of pollutants5 and molecular confinement studies5–6 to mention a few. In the area of catalysis, mesoporous silica-supported reactions have been investigated for example, in wastewater treatment7, in reducing the amount of certain compounds in the mainstream of tobacco smoke8 and in product yield improvement for organic reactions9–11 among other applications. In a particular case, copper doped nanoporous silica have been found to be a reusable, regioselective catalyst for the cycloaddition reaction between a terminal alkyne and an azide through click chemistry.10,12 However, in some cases, the yields of reaction are very low and this is attributed to the low interaction between the hydrophobic reactants and the hydrophilic materials.

In this context, MCM-41 materials offer high surface area, ordered structure and thermal stability, but it fails in provid-

ing the correct hydrophobic/hydrophilic balance for an efficient interaction with most organic molecules. Frequently, even after post-grafting hydrophobic groups on the surface, this balance is not met due to a total transformation of the surface from hydrophilic to hydrophobic. A partial functionalization with this method has shown to produce inhomogeneous, rough surfaces with the majority of the grafted groups on the external surface or at the extremes or the pores.9,13,14 The co-condensation method has been conceived as an alternative to introduce hydrophobic groups to mesoporous silica materials yielding to a more uniform functionalization9,15. In this case, a silica precursor is condensed together with an organosilane. This method has been studied to introduce acid, basic and unsaturated groups in the walls of MCM-41-like materials so that they can be directly used for catalytic applications.14,16–18 Our aim was to control the hydrophobicity of organosilica materials for specific applications by introducing methyl or phenyl groups through co-condensation with methyltriethoxysilane (MTES) or phenyltriethoxysilane (PTES). Such an approach for the synthesis of organosilica molecular sieves19 has been much less investigated.

Here, lysozyme was chosen as a model to study the effect of the surface hydrophobicity in protein uptake. In addition, the supported copper (click) catalysis of the cycloaddition reaction between two hydrophobic reactants, benzyl azide and 4-bromo-1-butyn, in aqueous media instead of an organic solvent, was tested with the synthesized materials.

For the direct synthesis of mesoporous organosilica, we focused on obtaining a stable material with a highly ordered pore structure. In order to avoid the disruption of the honeycomb-like structure and based on previous research,20 the percentage of organosilane in the precursor mixture was kept under 20 mol%. The conditions of template washing by ethanol extraction were optimized to obtain a clean material without causing damages to the surface.

II. Experimental Section

Materials
Ocdecytrimethylammonium bromide (C12H6NB), Dodecytrimethylammonium bromide (C13H6NB), Tetraethyl orthosilicate (TEOS), methyltriethoxysilane (MTES), phenyltriethoxysilane (PTES), Ammonia (30%), Hydrochloric acid (37%) and Ethanol (99.98%) were purchased from Sigma-Aldrich.

**Direct Synthesis of modified MCM-41.**

MCM-41-type materials with different percentages of MTES or PTES were prepared. For each one, 4 mmol of the cationic surfactant CnTAB was dissolved in 72.0 ml of ultrapure water at 50 °C and was stirred vigorously during 1.5 h for complete dissolution, then the temperature was decreased to 35 °C and 4.8 ml of ammonia (30%) were added. The mixture was stirred for fur-ther 5 min. After the precursors’ mixture was added keeping a constant number of moles of Silicon (26.33 mmol). The final molar composition of the reaction mixture was (1 – x) TEOS: x MTES (or PTES): 2.4 NH3: 0.15 CnTAB: 152 H2O where x is the fraction of methyl- or phenyl-triethoxysilane that goes from 0 to 0.15 and n is the length of the alkyl chain of the surfactant. The reaction was allowed stirring, at rate of 300 rpm, during 3.5 h. The obtained white solid was washed twice with 40 ml of HCl 2%w/v and then with ultrapure water until reaching neutral pH.

Samples were named according to the template used and their fraction of MTES or PTES in the precursor mixture, as follows: C8-M7-Me for 0.93 TEOS/0.07 MTES, C8-M15-Me for 0.85 TEOS/0.15 MTES, C8-M7-Ph for 0.93 TEOS/0.07 PTES, all of them using C8,TAB as template, and C12-M7-Me for 0.93 TEOS/0.07 MTES using C12,TAB as template. Standard MCM-41 C8 and C12 were synthesized and washed under the same conditions for comparison.

For template removal, 100 ml of a solution of HCl (2%w/v) were added per gram of product and it was stirred for 25 min at room temperature. The solid was filtered and re-dissolved in a mixture of 200 ml of Ethanol 99% and 10ml of ultrapure water. This mixture was stirred at 50 °C during 3 h, then, the solid was filtered and dried in the oven at 60 °C during 24 h. Only for sample C8-M7-Ph an extra thermal treatment at 350 °C during one hour under nitrogen atmosphere was needed for complete template removal.

**Characterization.**

FTIR spectra of the samples were taken from 4000 to 400 cm-1, with a resolution of 2 cm-1, with a Bruker TENSOR equipped with a platinum ATR. Nitrogen and water vapor adsorption-desorption experiments were performed with ASAP 2020 Surface Area and Porosity Analyzer from micromeritics. Nanoporous silica samples were degassed under vacuum at 90 °C during 24 h. Nitrogen adsorption isotherms were taken at 77 K, and water vapor adsorption isotherms at 298.15 K. Thermogravimetric analyses were performed with a Q50 thermoanalyzer from TA Instruments, with controlled atmosphere under nitrogen flow, from ambient temperature to 850 °C with a temperature ramp of 10 °C/min. Small-angle X-ray Scattering patterns were collected using a Xcuss 2.0 HR SAXS/WAXS instrument from Xenocs with a Cu Ka (5 kV, 0.6 A). TEM Images were taken with a JEOL JEM-2010 high resolution transmission electron microscope, operating at 200 kV.

**Lysozyme trapping.**

Approx. 10 mg of the selected materials were mixed with 10 ml of a 0.5 mg/ml solution of lysozyme from chicken egg white, in a 10 mM phosphate buffer pH 7.4, during 4 h at room temperature. Then, the suspensions were centrifuged during 10 min at 15000 x g, 1 ml of the superna-tant was passed through a 0.2 μm filter and transferred to a quartz cell. The UV absorption was taken at 280 nm. The UV absorption spectra of the rinsing water were also taken to discard the loss of weakly bounded lysozyme. The solids were rinsed with water and dried under vacuum, the FTIR spectra of the lysozyme-rich materials was taken.

**Copper post-grafting.**

The addition of copper followed the protocol described by Nancy Brodie-Linder et al. 150 mg of the washed nanoporous silica materials were added to 40 ml of a 0.05 M solution of copper nitrate, previously adjusted to pH 10.5 with ammonia (30%), and stirred vigorously for 10 min. Immediately after, the solid was filtered and washed with ultrapure water until neutral pH. The obtained blue material was dried in the oven at 50 °C. The abovementioned procedure was also applied on the as synthesized samples (without removing the surfactant from the pores), in order to obtain materials with copper grafted only on the external surface.

**Catalytic tests.**

The protocol for the catalysis experiments of the click reaction using copper doped nanoporous silica was the same as published before. For all samples, Benzyl azide (67 μl) and 4-bromo-1-butylene (47 μl) were added to 2 ml of water containing the 8 mol% of copper supported in the different silica materials. Reactions were stirred during 22 h. After that time, the mixtures were vacuum filtered with a polycryla-mide membrane and the blue solids were rinsed twice with 2ml of ethyl acetate each time. After solvent evaporation, the conversion to 1-benzyl-4-bromoethyl-triazole was determined by 1H NMR.

**Neutron Backscattering Experiments.**

The backscattering spectrometer IN6B allows experiments with a high-energy-resolution ∆E = 0.75 μeV at FWHM (equivalent to 5 ns) with a neutrons wavelength λ = 6.3 Å, in a wave vector range of 0.2 to 1.9 Å⁻¹, however the data presented are the sum of the Q scans obtained at each temperature. Standard Si(111) monochromator and analyzer crystal setup were used here. The experiments were operated in two different modes: we have measured the scattered intensities in the elastic fixed window (EFWS) mode and in the inelastic fixed window mode (IIWS) at energy of 20eV and performed several temperature scans from 2K to 290K. A flat aluminum cell was used and filled with the 2 materials, MCM-C8-M15-Me and MCM-C8-M15-Me partly calcined, in a glove box to avoid water contamination. The samples were first rapidly cooled and then heated at a rate of 2K/min until 100K and at 0.8K/min from 100K to 290K to improve the statistics.

**III. Results.**

Template removal and incorporation of the organic groups in the mesoporous silica was verified by means of FTIR (Figure S1 in ESI). Nitrogen adsorption and desorption isotherms at 77 K for these samples are shown in Figure 1. For standard and methyl modified MCM-41 C18, results show a regular type IV adsorption isotherm. In the case of co-condensation of TEOS with MTES, it was observed an increase of surface area and pore volume with respect to MCM-41 C18 (See Table 1). On the other hand, the co-condensation with PTES produced a less organized material, evidenced by a spread capil-
lary condensation, slightly lower surface area and pore volume than MCM-41 C18.

Figure 1. Nitrogen adsorption-desorption isotherms at 77 K of MCM-41 C18 and mesoporous organosilica materials.

The late condensation at P/P₀ higher than 0.9 in samples MCM-41 C18 and C18-M7-Ph was attributed to condensation in the interparticle cavities when the size of the mesoporous silica grains are in the nanometer scale, as it was evidenced for C18-M7-Ph by TEM (Figure S3).

These results indicate that upon introduction of MTES at percentages up to 15%, the obtained organosilica maintain an ordered pore structure while increasing their hydrophobic character. To investigate the upper limit of the fraction of MTES in the precursors mixture that could yield an ordered, highly porous material, an extra sample was synthesized with 20% MTES. Results show that even though a high BET surface area (903 m²/g) is obtained, there is a significant decrease in the pore volume (0.486 cm³/g) of the material.

Likewise, sample C12-M7-Me was synthesized in order to explore the hydrophobic modification of small pore mesoporous silica, which is difficult to obtain by post-grafting methods. In this case, a high surface area material, with pore volume slightly lower than the MCM-41 C12 was obtained. The production of such small pore sized material with controlled hydrophobicity, like the one obtained in this work, could be of great scientific interest for molecular confinement studies.

It is worth noting that the affinity constant, C, calculated from the BET equation, decreased 31%, 49% and 61% with respect to the value of MCM-41 C18 (C = 112) for C18-M7-Me, C18-M15-Me and C18-M7-Ph, respectively. This parameter decreases with a decrease on the strength of the adsorbent-adsorbate affinity. Since induced dipole-dipole interactions govern this adsorption, the introduction of organic groups decreases the affinity of nitrogen towards the surface. Then, the observed drop of the C value within the same family of materials is another evidence of their increasing hydrophobicity.

Figure 2 shows the Small-angle X-Ray scattering patterns for the synthesized materials. The observation of three Bragg peaks indexed as (10), (11) and (20) confirm the 2D hexagonal structure p6mm of the standard, and methyl modified materials. The broadening of the (10) peak of the phenyl modified sample could suggest a higher polydispersity in the pore size.

Figure 2. Small angle scattering curves of MCM-41 C18 and mesoporous organosilica materials.

The lattice plane spacing dₜoo was calculated from the SAXS patterns and it is shown in Table 1. This parameter in combination with the pore volume obtained by nitrogen adsorption allowed the calculation of the pore diameter (Dₚore). This method has been found to be more precise for the determination of the size of small hydrophobic pores than other models that use exclusively nitrogen adsorption data. We found that up to 15% MTES or 7% PTES, the pore diameter does not change significantly with respect to MCM-41, while the post grafting method induces always a decreasing and less predictable size.

Figure 3. Water adsorption isotherms at 298.15 K of (a) MCM-41 C18, (b) C18-M7-Me, (c) C18-M15-Me and (d) C18-M7-Ph.
Table 1. Mean physical properties of the mesoporous organosilica materials.

| Sample          | $S_{\text{BET}}$ (m$^2$/g) | $V_{\text{pore}}$ (cm$^3$/g)$^a$ | $d_{10}$ (nm) | $D_{\text{pore}}$ (nm)$^b$ | Cu(II) (%w/w) |
|-----------------|-----------------------------|----------------------------------|---------------|----------------------------|---------------|
| MCM-41 C18      | 1007                        | 0.712                            | 4.45          | 4.22                       | -             |
| C18-M7-Me       | 1130                        | 0.899                            | 4.48$^d$      | 4.43                       | -             |
| C18-M15-Me      | 1284                        | 0.982                            | 4.31          | 4.32                       | -             |
| C18-M20-Me      | 903                         | 0.447                            | 4.05          | 3.46                       | -             |
| C18-M7-Ph       | 989                         | 0.628                            | 4.65          | 4.30                       | -             |
| MCM-41 C12      | 979                         | 0.539                            | 3.55          | 3.17                       | -             |
| C12-M7-Me       | 1134                        | 0.505                            | 3.37          | 2.97                       | -             |
| Cu/MCM-41 C18   | 308                         | 0.286$^b$                        | -             | -                          | 14.5          |
| Cu/C18-M7-Me    | 256                         | 0.181                            | 4.46          | 2.89                       | 9.8           |
| Cu/C18-M15-Me   | 377                         | 0.227                            | 4.32          | 3.02                       | 9.9           |
| Cu/C18-M7-Ph    | 430                         | 0.331                            | 4.55          | 3.58                       | 9.9           |

$^a$ Single point adsorption total pore volume at P/P$_0$ = 0.5.
$^b$ Single point adsorption total pore volume at P/P$_0$ = 0.8.
$^c$ Not measured.
$^d$ Calculated using the KJS model taking into account the lattice plane spacing ($d_{10}$).

Water adsorption isotherms (Figure 3) show that the total quantity of water increases when the pore volume of the material is higher, regardless of their organic functionalization. These results show that the hydrophobicity of the materials is not strong enough to avoid water vapor condensation in the pores.

The stability of the materials towards hydrolysis was studied by performing nitrogen adsorption analysis before and after water adsorption. Results (Figure S2) clearly show that samples C18-M15-Me and C18-M7-Ph are better stabilized, with a smaller loss of pore volume than C18-M7-Me. The water-resistance found here, could be crucial for better performance of the molecular sieves in aqueous solution.

Transmission electron microscopy images of selected samples are shown in Figure S3. Both C18-M7-Me and C18-M7-Ph show the highly ordered, hexagonal structure, surrounded by mesocellular silica foam (MCF), reported before when 1,3,5-trimethylbenzene was incorporated to the synthesis of the mesoporous silica$^{34}$. A possible explanation is that MCF rises due to the formation of a microemulsion upon addition of the organosilane, which behaves as a swelling agent, due to its hydrophobic character. The abundance of MCF structures in C18-M7-Ph explains the increased width of the Bragg’s peaks in the SAXS pattern for this sample.

Additionally, in order to verify the presence of methyl groups at the surface of the pore, we have conducted quasielastic neutron scattering experiments in the fixed elastic mode window mode of 2 μE. From the T-dependent of the elastic scans obtained, we could identify a pronounced enhanced mobility of the methyl groups starting at 80K.

We have investigated the presence of methyl groups at the surface and in the wall of MCM-C18-M15-Me and distinguished the onset of their free rotation about the threefold axis as temperature increases from 2K to 290K. For that purpose Incoherent Neutron Backscattering method is particularly well suited because of its high sensitivity to Hydrogen atoms and its possibility to operate Elastic and Inelastic Fixed Window temperature Scans, EFWS and IFWS, which can easily identify the onset of motions faster than few nanoseconds. With the high resolution backscattering spectrometer IN16B at the ILL (Grenoble, France)$^{35}$, we have performed two sets of experiments$^{26,27}$ on two different samples. The first sample is the C18-M15-Me, compared to its partly calcined homologue, the latter being heated up to 550°C in order to suppress a large part of the methyl groups attached at the surface. The results are presented in Figure 4 (a, b) where respectively the two IFWS and their intensity difference are reported.
comes from the aromatic C-C stretch of the phenyl functionalization. The amide I band consists of C=O stretching coupled with N-H bending and C-H stretching components. As these stretching modes are affected by the hydrogen bonds present in the different conformations (α-helix, parallel and antiparallel β-sheets, etc.), the shape of the amide I band gives information about the secondary structure of the protein\(^{38}\). It is then possible to perform studies of protein structure under different confined conditions using these new molecular sieves.

![Figure 5](image.png)

**Figure 5.** (a) Quantity of Lysozyme adsorbed from a 0.5 mg/ml solution at pH 7.4, per milligram of material (b) FTIR (ATR) Spectra of the lysozyme adsorbed on the materials. Insert: Zoom of the amide I and II bands of lysozyme.

### Catalysis of the alkyn-azide cycloaddition reaction

The azide-alkyne cycloaddition reaction at ambient temperature, as shown in figure 6, typically requires a copper (I) species as catalyst. This species is prompt to disproportionate, making it necessary to add an auxiliary reducing species, as ascorbate, to have an efficient catalysis. Additionally, an extraction or filtration step has to be performed to purify the product\(^{39}\). Another alternative is to use copper loaded on nanoporous silica for heterogeneous catalysis.\(^{12}\)

![Figure 6](image.png)

**Figure 6.** Cycloaddition reaction between bromobutyne and benzylazide in the presence of a copper catalyst in water.
Copper (II) was immobilized on the materials using the method developed by Brodie-Linder et al.\textsuperscript{11} N\textsubscript{2} adsorption isotherms for the copper post-grafted materials (Figure 7) show a lower total amount adsorbed than the pristine samples.

![Graph showing nitrogen adsorption isotherms](image)

**Figure 7.** Nitrogen adsorption isotherms at 77 K (up) and yields of the cycloaddition reaction between bromobutyne and benzyl azide in water (down) for the different silica-supported copper catalysts.

The irregular shape of the isotherm of Cu/MCM-41 C18 indicates more important wall degradation due to the contact with the basic copper solution. In this sense, the organic groups seem to protect the surface from basic hydrolysis, same as observed after water adsorption, Cu/C18-M7-Ph being the least affected in terms of surface area and pore volume. There is also an expected decrease on the pore size in all samples due to the incorporation of copper on the surface.

The materials were tested as catalysts for this reaction, with no addition of reducing agents or further ligands. Figure 7 shows the yields of reaction obtained by means of NMR spectroscopy. A vast increase in the yield of reaction is observed for the methyl- and phenyl-modified samples Cu/C18-M7-Me, Cu/C18-M15-Me and Cu/C18-M7-Ph (87%, >99% and 78% respectively) with respect to the yield of 11% obtained when Cu/MCM-41 C18 is used as catalyst. These results confirm that the surface area and the organic functionalization of the materials play an important role in the efficiency of the catalyst. In this case, the presence of methyl or phenyl groups enhances the adsorption of the organic reactants. Another important factor is the pore diameter of the catalyst. It has been observed before that a tight fit that allows the entrance of the targeted molecules while also providing a confined environment for the reactants to interact, is a key factor in obtaining high reaction yields. Total transformation of the reactants on Cu/C18-M15-Me (pore size of 3.02 nm and a surface area of 377 m\(^2\)/g) indicates that this material provides an optimum hydrophobic nanoenvironment for this particular reaction in water. A control experiment using copper-doped materials with pores blocked by surfactant (Figure S4) allowed confirmation that most of the conversion takes place inside the pores of the hydrophobically modified materials.

**Conclusion**

By means of a direct synthesis of TEOS with MTES or PTES, mesoporous organosilica materials were synthesized with different degrees of hydrophobicity for testing their applications in lysozyme trapping and supported copper catalysis. A complete characterization confirmed the large surface area, ordered pore structure and organic functionalization of the materials, providing a partial hydrophobic environment that depends on the percentage of organosilane present in the precursor mixture. It was observed that such a difference in the nanoenvironments had a significant impact on the performance of the materials in the selected applications.

The quantity of lysozyme adsorbed decreased for all the methyl-modified materials, with respect to the original MCM-41 C18. In contrast, the lysozyme uptake by the phenyl-modified sample, C18-M7-Ph, was more than three times higher than the reference MCM-41. This enhancement is attributed to \(\pi-\pi\) interactions between the organosilica and the protein.

The copper doped materials were proven to be active for regiospecific catalysis of the cycloaddition reaction between bromobutyne and benzyl azide, using water as solvent. In particular, C18-M15-Me has provided an ideal surface for this specific reaction, with an obtained yield of reaction of >99%. These unprecedented results for a Cu (II) supported catalyst, using such a facile synthesis encourages the testing of the materials for the synthesis of further triazole derivatives in water.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

FTIR spectra, N\textsubscript{2} adsorption isotherms before and after water adsorption, TEM images and yields of catalysis reaction with blocked pores (PDF).

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