Influence on the SBA-3 Structure by Alkaline or Alkaline Earth Ions

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Alkaline and alkaline earth cations have been used in the synthesis of SBA-3, a silica mesoporous materials. These cations can not substitute silicon in the silica structure. However, we found that SBA-3 surface area, pore size and thickness, periodic order, and microporosity were affected by the presence of lithium, magnesium, or calcium ions. Chemical interactions among these ions and silica species are supposed to occur on the SBA-3 pore surface.

Mesoporous materials consist of long-range-ordered inorganic arrays with pores in the range 2–50 nm in diameter. They have numerous applications in synthesis, material science, and many other fields. Their synthesis is of considerable interest and is constantly being developed to introduce different properties.[1] The principles of the formation of silica mesoporous materials from templating micelles are known.[2] Consequently, their structure can be modified varying parameters such as pH, temperature, surfactants, silica precursor, etc.[1,2] Among them it has been observed that inorganic anions influence the pore size, and a correlation with the anion position in the Hofmeister series has been proved.[3] No studies have been presented on the influence of inorganic ions.

In this research, we have studied how the structural features of SBA-3, silica mesoporous materials obtained in acid environment, were affected by the presence of high concentrations of alkaline and alkaline earth cations (Me). It is known that they influence micelle formation, shape and interaction,[4] and silica species polymerization.[5] These metal cations can not substitute silicon in the SBA-3 structure[6] and thus should be mainly located at the micelle–silica interface. The syntheses of SBA-3 have been carried out in the presence of lithium, sodium, magnesium, or calcium chloride. Metal ion/silicon molar ratio (Me/Si) was equal to 1, 3, or 8. SBA-3 formed at Me/Si equal to 1 or 3. At Me/Si equal to 8 silica amorphous material precipitated. This could be related to an alteration of the templating micelle structure induced by the high concentration of electrolytes.[4] Diffraction patterns of calcined SBA-3 are shown in Figure 1. They were indexed as hexagonal mesophase.[7] The SBA-3 lattice parameter, a_0, did not change with respect to the control in the presence of Na^+, while reduced in the presence of Mg^{2+}, Ca^{2+}, or Li^+ (Table 1SI).[14] SBA-3 syntheses have been carried out below the isoelectric point of silica (pH 2).[5] In this condition, chloride ions mediate the electrostatic interactions between the positively-charged surfactant head groups and silica oligomeric species, which ensure the SBA-3 formation.[2,7] The presence of Me causes a decrease of the double electric layer thickness surrounding the micelle.[5,8] As consequence, the template curvature increases and the pore diameter of the mesoporous material decreases.[8] The influence of Me should be associated to their charge density and hydration sphere, being the counter anion always the same. Indeed Mg^{2+} is able to reduce SBA-3 pore size more than Ca^{2+} and the latter more than Li^+, and the effect becomes more pronounced increasing the Me concentration (Table 1SI).[14] SBA-3 calcination process provokes a reduction of the lattice parameter, Δa_0, due to the thermal polymerization of unreacted silica species.[9,10] It was observed that Δa_0 was higher in the presence of Li^+ and lower in the presence of Mg^{2+} (or Ca^{2+}) with respect to the control, suggesting higher and lower concentrations of unreacted silica species, respectively. Na^+ did not affect the calcination process (Table 1SI). Li^+ may reduce the silica species polymerization forming hydrogen bonds with silanol groups.[5] On the contrary, Mg^{2+} and Ca^{2+} stabilize the SBA-3 against calcinations, probably forming ionic bonds with silicate species.[11] The same ions increased the coherence length of SBA-3, which was estimated by full width half maximum diffraction peak (001) (Table 1SI).

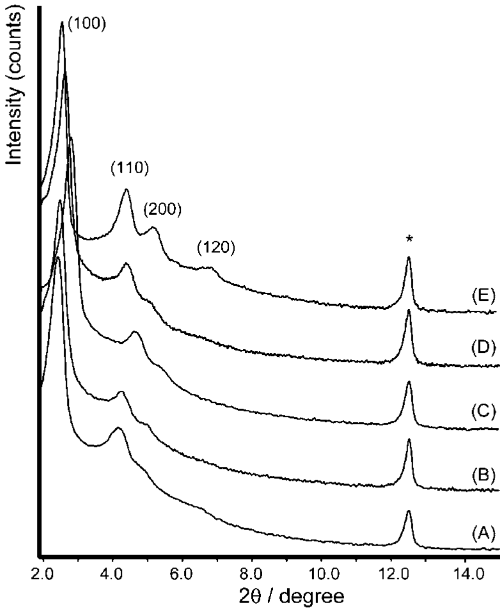

Figure 1. Powder X-ray diffraction patterns of calcined SBA-3 synthesized in the absence (A) and the presence of Me (B)–(D) from solutions having Me/Si equal to 3. (B) Na^+; (C) Li^+; (D) Ca^{2+}; (E) Mg^{2+}. * indicates the (012) diffraction peak of chrysotile, which was used as internal standard. All the diffraction patterns were normalized to the intensity of (100) diffraction peak and displaced along the vertical axis.

FTIR spectra of as-synthesized SBA-3 show absorption bands at 1500–1450, 915, and 730–720 cm^{-1} associated to the surfactant and at 1230, 1160, 1080, 960, 800, 560, and 460 cm^{-1} associated to the silica species (Figure 2I). The band at 1630 cm^{-1} can be attributed to the presence of adsorbed water molecules. The FTIR spectra from calcined materials show only

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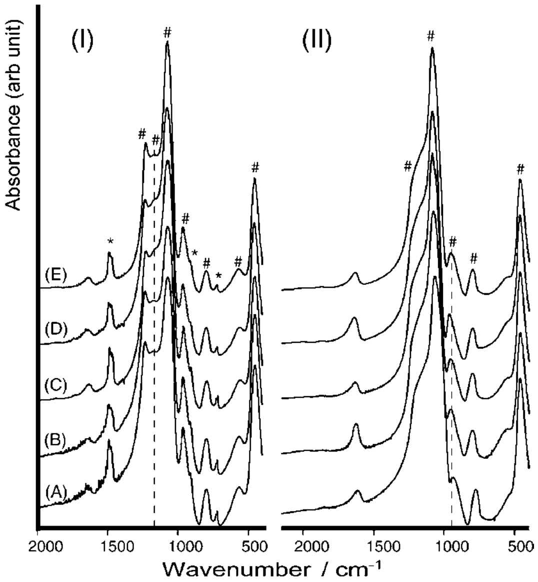

Figure 2. FTIR spectra of SBA-3 collected from as-synthesized (**I**) and calcined (**II**) samples. SBA-3 prepared in the absence (A) and presence Me (B)–(E) from solutions having Me/Si equal to 3. (B) Na^+; (C) Li^+; (D) Ca^{2+}; (E) Mg^{2+}. (#) and (*) indicate the bands associated to the silica species and to the surfactant, respectively. All spectra were normalized to the intensity of the band at $1080\,cm^{-1}$ and were displaced along the vertical axis that reports absorption in arbitrary units. The dashed lines indicate the absorption bands at 1160 and $960\,cm^{-1}$.

the bands due to the silica species, with a shift of the band 1080 to $1090\,cm^{-1}$.

The key stages in the silica species polymerization processes are shown by the change in the relative intensity of the bands at 1160 and $1080\,cm^{-1}$, which are assigned to the internal Si–O vibrations and groupings, respectively.[12] In the as-synthesised SBA-3 materials the band intensity at $1160\,cm^{-1}$ increased or decreased with respect to the control in the presence of Li^+ or Mg^{2+} (Ca^{2+}), respectively (Figure 2I). This suggests that Li^+ stabilizes and Mg^{2+} or Ca^{2+} destabilize silica precursor species with respect to the control, in agreement with the XRD data. The FTIR spectra of the calcined samples show that in the presence of Mg^{2+} or Ca^{2+} there is a stronger absorption of the band at $960\,cm^{-1}$ with respect to the control (Figure 2II). This band has been associated to the presence of hydrated magnesium (or calcium) silicate.[13] This observation fits with the change of Δa_0 associated to the calcination processes that supposed the formation of silicates on the SBA-3 pore surface. The amount of Me hosted by the SBA-3 is very low (Table 1SI). This data was expected since Me cannot substitute silicon in the silica structure and should be present as intercalate and/or bounded on the pore surface. The fact that Mg^{2+}, Ca^{2+}, and Li^+ are present in higher amounts with respect to Na^+ is in agreement with the above observations. The elemental analysis of the samples did not show the presence of any additional ions and stoichiometric silica precipitated.

The N_2 adsorption measurements were used to evaluate the area surface and the average pore diameters (Table 1SI).[14] The pore wall thickness, t, was estimated as the difference between a_0 and the pore diameter obtained from N_2 adsorption measurement. The data show that the wall pore thickness slightly increased in the presence of Mg^{2+} or Ca^{2+}, while in the presence Li^+ or Na^+ did not change significantly with respect to the control. The supposed chemical interactions between Mg^{2+} (or Ca^{2+}) and silica species should justify this behavior, provoking a lower reduction of the wall thickness due to the calcination process with respect to the control. The SBA-3 microporosity was roughly estimated from surface area data.[5] It did not change in the presence of Na^+, while in the presence of Li^+, Mg^{2+}, or Ca^{2+} increased with respect to the control (Table 1SI).[14] These data do not correlate with the SBA-3 materials pore size and the wall pore thickness. In fact in the presence of Mg^{2+} or Ca^{2+} the pore size decreases and the wall thickness increases suggesting a decrease of the surface area. Thus, we suppose that the SBA-3 microporosity should increase with respect to the control in the presence of Mg^{2+} or Ca^{2+}.

In conclusion these studies show that SBA-3 structural and textural features can be modified by the presence of alkaline or earth alkaline ions and that during the synthesis chemical interactions take place on the pore surface among these cations and silica species.

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