A novel methodology for the synthesis of silicon oxide mesoporous materials has been developed using soft reaction conditions, unlike other synthesis conditions present in the literature. The synthesis involves the use of the lyotropic liquid crystals formed by mixing the surfactant hexadecyltrimethylazanium (CTAB), sodium nitrate as catalyst, water and tetraethyl orthosilicate (TEOS) as the inorganic precursor. The silicon oxide samples were characterized by high-resolution transmission electron microscopy (HRTEM) and EDX analysis. The specific surface area of the powder and the pore size were determined by the BET method and were found to be 587 m$^2$/g and 2-4 nm, respectively. The point of zero charge (pzc) determination using a zeta-meter apparatus was 3.1 showing the acid character of the surface. The template mesoporous SiO$_2$ samples can be used to prepare composite electrodes containing active mixed oxides, e.g. for lithium-ion batteries.

**INTRODUCTION**

The synthesis of new nanostructured materials is a field in constant development because at that size scale the physicochemical properties of matter change significantly. Indeed, different nanostructures have been synthesized, including nanowires, nanotubes and nanopores. There are different synthesis methods to prepare these nanomaterials, the most common being the chemical vapour deposition (CVD), thermal decomposition of precursors, co-precipitation, sol-gel, microwave, electrochemical methods, and chemical solvothermal synthesis. It is well known that the synthesis of nanostructures is possible using templates. Different supramolecular structures, e.g. lamellar, hexagonal, and cubic or smectic mesophases, can be used as templates. They can be obtained on the basis of surfactant/water or polymer/water mixtures. Lin et al. have functionalized these compounds, which allowed the design of nanometric scale containers that can be used as carriers for molecules of biological interest, such as therapeutic proteins, enzymes and polynucleotides. In the battery field, Wu et al. have prepared mesoporous of titanium using templates as anodes for lithium-ion batteries, improving their charge-discharge cycle characteristics. More recently, Wang et al. have developed three methods for the synthesis of mesoporous SiO$_2$ hollow spheres with uniform pore diameter of 3.6 nm to 3.8 nm. These hollow spheres allow the encapsulation of different types of metals (Au, Ag), semiconductors (ZnS, TiO$_2$, Co$_3$O$_4$, Fe$_3$O$_4$) and conductive polymers (polyaniline).

In general, the route to obtain mesoporous materials involves the use of supramolecular structures (templates) and a strong acid medium, high temperatures and pressures. These parameters directly influence the properties of the obtained mesoporous materials, such as type of structure, morphology, specific surface area, pore size and thickness of the wall. Additionally, other factors has been considered: the surfactant concentration, the surfactant/inorganic precursor ratio and the acidity of the medium. Xiao et al. studied the effect of the temperature on the synthesis of mesoporous silica nanofibers obtained at 283 K exhibiting a specific surface area of 952 m$^2$/g. As the temperature increased from 283 K to 293K and to 308 K, the specific surface areas of the mesoporous system decreases to 656 m$^2$/g and 462 m$^2$/g respectively.

J.H. Zhu et al. studied the effect of the molar ratio TEOS/HNO$_3$ ratio on the ordering degree of the mesoporous obtained. These authors have found out that when the molar ratio TEOS/HNO$_3$ exceeds 3.5, the mesophase loses its structural order. Another conclusion of this work is related to the absence or presence of phenol in the mixture. It was determined that when the CPyCl to phenol molar ratio is 1:1, the generated mesophase is cubic, while in the absence of CPyCl the mesophase is hexagonal. Meanwhile, when the ratio is 1:2, lamellar silica is obtained.

In this work, we present a methodology for the synthesis of silicon oxide mesoporous materials under soft reaction conditions, namely one atmosphere, 313 K and pH = 7. The synthesis involves the use of a lyotropic liquid crystal as the template, as suggested by Xiao et al.
only silicon and oxygen.

Figure 1. HRTEM images series for the sample m-SiO$_2$.

Figure 2. STEM-HAADF and EDX measurements for the sample synthesized under conditions previously mentioned.

BET measurements are used primarily to determine the pore diameter with surface area. Moreover, this measure allows us to obtain a classification of the pore size, since the shape of the adsorption isotherm allows to catalog the compound obtained as micro-, meso or macroporous. Figures 3A and 3B show the curves obtained by BET measurement, allowing to obtain the above parameters. Figure 3A shows the pore diameter distribution as a function of pore volume, as can be appreciated the majority pore diameter is in the range of 2 nm to 4 nm. On the other hand, Fig. 3B shows a typical IV adsorption isotherm type characteristic of mesoporous solids, with a hysteresis loop associated with tubular capillaries open at both ends. From this isotherm it was possible to obtain the surface area of SiO$_2$, whose calculated value was 587 m$^2$/g. This relatively high value indicates a high density of pores available for using SiO$_2$ as template. From these results it is possible to confirm the formation of mesoporous structures.

Figure 3. BET analysis of mesoporous silicon oxide. A) Pore volume vs. pore diameter, B) volume of gas adsorbed vs relative pressure.

Furthermore, to characterize the charge on the surface of the mesoporous silicon oxide, we determined the isoelectric point as a function of pH. Figure 4 shows the results for two measurements. In both cases the intercept of these curves with the pH axis present the same value for the point of zero charge, pzc, at pH 3.1 indicating that their surface is positively charged. This parameter is important to expand the scope of the use of silicon oxide as the template, to manufacture, for example, mixed oxide electrodes for lithium-ion batteries, since most of the oxides used in the manufacture of these devices are formed from negatively charged precursors. Therefore, positively charged surfaces favor the encapsulation of these precursors within the template.

To the previously stabilized liquid crystal solution, the inorganic precursor is added, and the system is allowed to react for 24 hours. The calcination of the material takes place under conditions of controlled temperature, as described above, because the nanostructure collapses under more severe conditions.

According to Xiao et al.\textsuperscript{8}, the concentration of the NO$_3^-$ ions plays an important role on the catalytic hydrolysis of TEOS and the formation of the final nanostructure. In fact, depending on the NaNO$_3$/TEOS molar ratio used, the particle morphology that is obtained changes from aggregate particles (NaNO$_3$/TEOS = 0.3) to fiber (NaNO$_3$/TEOS = 1). The role of the NO$_3^-$ can be explained on the basis of the NO$_3^-$ anion having a high binding selectivity in relation to the cationic surfactant CTA and leading to long cylindrical micelles which would facilitate the formation of the nanostructure\textsuperscript{8}. Currently, we are conducting work to clarify this further.

CONCLUSIONS

Silicon oxide mesoporous materials can be easily prepared using a soft template route which involves the initial formation of the liquid crystal with CTAB in water using NaNO$_3$ as the catalyst, followed by the addition of TEOS at pH = 7, one atmosphere and 313K. This technique appears as very convenient when compared with others, which are used under very extreme experimental conditions of acidity, temperature and pressure. The mesoporous silicon oxide thus synthesized shows a low distribution of pore sizes, between 2 to 4 nm. Such mesoporous material can be used as a template in the manufacture of battery electrodes, sensors, optoelectronic devices and catalysts.

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