

Synthesis of porous silicas with high surface area using renewable templates

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ABSTRACT

Porous silica have attracted great interest as supports in heterogeneous catalysis because they show very high specific surface areas and pore volume, and offer the possibility of incorporating a variety of heteroatoms. Non-ionic templates have been traditionally used for the synthesis of mesoporous silicas but they have drawbacks such as high cost and non-renewable nature. In this work we evaluated the use of templates that are renewable, cheap and highly available, specifically glycerol and glycerol monostearate. Tetraethylorthosilicate was employed as the silica precursor while ethanol, isopropanol and a water-ethanol mixture were used as solvents. The results show that glycerol induces microporosity while glycerol monostearate induces mesoporosity, but this latter template requires the presence of glycerol for its stabilization. Ethanol was the best solvent. Some of the obtained silicas exhibit ideal surface characteristics for a potential application as supports in heterogeneous catalysis.

Keywords: glycerol, glycerol monostearate, porous silica, solvent, tetraethylorthosilicate (TEOS).

1 INTRODUCTION

Silicas are important supports in heterogeneous catalysis because they have very high specific surface areas, large pore volumes and offer the possibility of incorporating a variety of chemical moieties or heteroatoms within their structure or surface, which act as catalytically active species [1].

The formation of porosity in the silica is achieved by the addition of templates to the synthesis mixture, in which the interaction between free silicates and template leads to the formation of hybrid micelles. The presence of such micelles makes the excess silicates react with one another to give rise to the formation of siloxane bonds around them, resulting in a siliceous material formed with an organic skeleton. The removal of the template by non-corrosive solvent extraction or calcination, gives rise to a porous solid structure based on channels defined by walls of silica [2-6].

Non-ionic templates such as Triton X-100 ($C_8H_{17}(C_6H_4)(EO)_{10}H$), Brij56 ($C_{16}H_{33}(EO)_{10}H$) y Pluronic F108 (PEO-PPO-PEO) have been traditionally used for the synthesis of porous silicas [7,8], these templates have critical drawbacks like their high cost and non-renewable nature. Therefore, in this work it was investigated the use of

templates that are renewable, cheap and highly available, specifically glycerol (Gly) and glycerol monostearate (ME). These substances are derived from fats and oils, they are not toxic and are environmentally friendly due to their high biodegradability. Tetraethylorthosilicate (TEOS) was employed as the silica precursor while ethanol, isopropanol and a water-ethanol mixture were used as solvents. The conditions for the removal of template, by calcination, were determined by thermal analysis (TGA-DTA). Morphological and textural characteristics were determined by nitrogen physisorption analysis and scanning electron microscopy..

2 EXPERIMENTAL

2.1 Treatment of silica precursor

The hydrolysis of the silica precursor was carried out by adding TEOS to a solution of hydrochloric acid ($pH = 2$) under strong magnetic stirring. The agitation was kept until the emulsion formed with the solvent was completely removed, rendering a homogeneous and translucent solution. Ultimately, the pH of the solution was adjusted to 3 using a 1 M solution of sodium hydroxide.

2.2 Synthesis of silicas

Glycerol (Gly) and glycerol monostearate (ME) were dissolved in a Teflon reactor containing the solvent at room temperature with gentle magnetic stirring. Then the silicate solution, previously prepared, was added and the stirring was maintained for 60 minutes to achieve a homogeneous mixture. The mixture was placed in a preheated oven at $60^\circ C$ for 24 h. After this period, sodium fluoride (NaF) was added to initiate the condensation reaction of silica and the mixture was heated at $60^\circ C$ for 7 days. After this stage, the material was dispersed by ultrasound, filtered, washed with solvent and dried at $80^\circ C$ for 12h.

The template incorporated in the structure of silica was removed by calcination in air at a heating rate of $1.5^\circ C/min$ up to $550^\circ C$ and held at this temperature for 4 hours. The so-obtained silica was characterized by SEM and nitrogen physisorption.

2.3 Hydrothermal stability

The silica was placed in contact with boiling water for 8 hours. After this period, the silica was filtered and dried at 80°C for 12 hours.

3 RESULTS AND DISCUSSION

Table 1 shows the specific surface area (BET method), total pore volume and pore size (BJH method) for all the synthesized silicas. It is clear that both templates, glycerol (Gly) and glycerol monostearate (ME), as well as the type of solvent have great influence on the textural characteristics of the porous silicas.

Table 1. Surface characteristics of silica.

Sample*	S	V	D
SiO ₂ (2:1:2)-E	505	0,631	45
SiO ₂ (2:1:10)-E	478	0,535	45
SiO ₂ (2:1:20)-E	607	0,602	47
SiO ₂ (1:1:1)-E	601	0,274	27
SiO ₂ (1:1:5)-E	649	0,352	29
SiO ₂ (1:1:10)-E	824	0,336	26
SiO ₂ (2:3:2)-E	711	0,926	46
SiO ₂ (2:3:10)-E	714	0,920	45
SiO ₂ (2:3:20)-E	727	0,915	44
SiO ₂ (2:1:2)-I	693	0,645	39
SiO ₂ (2:1:10)-I	669	0,381	28
SiO ₂ (2:1:20)-I	582	0,278	27
SiO ₂ (1:1:1)-I	398	0,668	55
SiO ₂ (1:1:5)-I	534	0,453	36
SiO ₂ (1:1:10)-I	564	0,347	30
SiO ₂ (2:3:2)-I	559	0,231	29
SiO ₂ (2:3:10)-I	623	0,502	54
SiO ₂ (2:3:20)-I	640	0,278	27
SiO ₂ (2:1:2)-W	540	0,514	35
SiO ₂ (2:1:10)-W	723	0,396	30
SiO ₂ (2:1:20)-W	736	0,410	36

Synthesis conditions: 60°C, 7 days under autogenous pressure. S: surface area (m²/g), V: total porous volume (cm³/g), D: average pore diameter (Å). E: ethanol, I: isopropanol, W: water-ethanol. *Values in parenthesis denote SiO₂:ME:Gly molar ratios.

3.1 Solvent effect

As for the effect of type of solvent, the surfactant had an adequate solubility in ethanol and isopropanol. For the water-ethanol mixture, the ME exhibited limited solubility in the solvent. This is because the HLB (hydrophilic-lipophilic balance) of ME, with a value of 3.8, is quite low in the scale of Griffin, which means that this substance has

a fairly strong lipophilicity, which limiting their interaction with the water in the reaction mixture. This effect is moderately neutralized with the addition of Gly to the mixture, and only syntheses with molar ratio Si: ME 2:1 were possible. Ethanol, which has a more moderate polarity than the water-ethanol mixture, allowed appropriate interactions between surfactants and silica precursors that gave rise to quite suitable mesoporous materials for heterogeneous catalysis. The best silicas were obtained with this solvent. Of the three solvents, isopropanol is the one with the higher organic load, which makes the polarity of the mixture even more moderate and improves the diffusion of ME in the mixture. Atypical results were observed with this solvent, compared to those observed with ethanol and water-ethanol. This suggests that the use of solvents with polarity lower than that of ethanol significantly affects the interactions of the micelles with the silica precursors.

Based on this, as well on the results shown in table 1, it is possible to suggest that the polarity of ethanol is the most convenient for the synthesis of mesoporous silica, using ME and Gly as surfactants, because ethanol has no solubility limitations of the surfactants.

3.2 Effect of surfactants in ethanol

For ethanol synthesis, in general, the BET surface area tends to increase with increasing concentration of surfactants, both Gly as ME. This effect can be explained as follows: with increasing concentration of surfactants increases the likelihood of greater amount of organic material is trapped by the network of siloxane (-Si-O-Si-), which causes it to generate a greater number of channels in the resulting solids. Silica SiO₂(2:1:10)-E was the only one showing an atypical to this general trend.

Considering the volumes and average pore diameters, there is not a strong trend that is related to the concentration of surfactants. The pore volume varies significantly with the concentration of ME and very gently with the concentration of Gly. This is evident when comparing the values for the groups of silica SiO₂(2:1: x)-E, SiO₂(1:1: x)-E and SiO₂(2:3: x)-E. In each group, silica exhibited very close pore volumes, indicating that the effect of the variation in Gly expressed as the variation of x is very subtle, but when comparing the average values for each group, 0.589, 0.320 and 0.921 cm³ / g respectively, can be seen very significant differences. Although there are no clearly defined trends relating the pore volume with the concentration of ME, the pore volume obtained for the silica group with the highest concentration of ME is markedly different from the others. The concentrations of surfactants affect very subtly the average diameter of pores for both the Gly and for the ME.

For the group of silica SiO₂(2:3: x)-E, which corresponds to the synthesis that involved the highest concentration of ME, by increasing the concentration of

Gly increases the BET surface area while the total pore volume and diameter through pores decrease.

3.3 Effect of surfactants in isopropanol

When using isopropanol as a solvent, the effect of the concentration of ME has a strong effect on the behavior of the micelles. As noted in Table 1, using this solvent was found that the higher BET areas were obtained with lower concentrations of surfactants, contrary to what was observed with other solvents. As the combined effect of the concentration of ME and Gly, for the group of silica $\text{SiO}_2(2:1: x)\text{-I}$, which corresponds to the synthesis with the lowest concentration of ME, by increasing the concentration of Gly decrease surface area, total pore volume and average diameter of pores. In the group of silica $\text{SiO}_2(1:1: x)\text{-I}$, which corresponds to the average level synthesis with the concentration of ME, as it increases the concentration of Gly the area increases, while the total pores and average pore diameter decrease. For the group $\text{SiO}_2(2:3: x)\text{-I}$, which corresponds to the maximum level of concentration of ME, the area tended to increase with the concentration of Gly, while the total pore volume and pore average diameter did not exhibit a clearly defined trend. In general, only the group of silica $\text{SiO}_2(2:1: x)\text{-I}$ showed a tendency to decrease the area with increased concentrations of Gly. Other groups, $\text{SiO}_2(2:1: x)\text{-I}$ and $\text{SiO}_2(1:1: x)\text{-I}$, showed a similar effect to the general trend described by the other silicas obtained with the other solvents in terms of increase in area with the concentration of Gly. Regarding this phenomenon, it may be suggested that the lowest concentration of ME is very close to a critical micelle concentration (CMC), which is a point where an abrupt change occurs in the structural characteristics and behavior of the micelles formed in the solvent. The CMC was disrupted by the addition of Gly making the micelles disappear in part, change shape or disperse in the solvent. This affected the meso-structural features of materials. The volume and pore diameter for groups of silica $\text{SiO}_2(2:1: x)\text{-I}$ and $\text{SiO}_2(1:1: x)\text{-I}$, decrease with increased concentrations of Gly. The group $\text{SiO}_2(2:3: x)\text{-I}$ did not describe a clearly defined trend.

3.4 Effect of surfactants in water-ethanol

Despite the limited solubility of ME in water-ethanol solvent, the obtained silica showed quite good textural characteristics, as can be seen in Table 1. In this synthesis, the surface area shows a tendency to increase as it increases the concentration of Gly. The total pore volume and average diameter of pores do not show a clearly defined trend with the variation of the concentration of Gly. The silica $\text{SiO}_2(2:1:10)\text{-W}$ and $\text{SiO}_2(2:1:20)\text{-W}$ exhibited areas fairly close, being higher those involving the largest concentration of Gly. Increasing the concentration of glycerol, besides contributing subtly to increase the surface area, favors the formation of more homogeneous and stable

micelles, which eventually provided more uniform porous characteristics of the resulting material. This effect of the concentration of Gly on the surface characteristics is attributed to the great similarity of the water due to its polarity. This makes the Gly completely disperse in the environment by increasing the organic load and subtly decreasing the polar character of the solvent, favoring the inclusion of ME in the medium and its interaction with silica precursors. Since this silica was synthesized with a low concentration of ME, the high concentration of Gly present in the environment, besides contributing to stabilize the ME micelles, leads to smaller and independent micelles with other molecules of Gly, resulting in to the formation of micropores.

3.5 Morphological Characteristics

Micrographs of silicas (not shown) show that the surfactants studied (ME and Gly) lead to the formation of agglomerates of particles completely amorphous and irregular. Silica with these characteristics would not apply as stationary phases in high-performance liquid chromatography (HPLC) or as an abrasive material for chemical-mechanical surface treatment (mirror finish), where the particle shape plays a very important role. In heterogeneous catalysis the morphology of the particles of the support is not a key variable, while the surface area and the accessibility of reactants to active sites are very important features. Several of the silica developed in this research have great potential for the latter application, for example the group of silica $\text{SiO}_2(2:3: x)\text{-E}$.

3.6 Hydrothermal stability

As a very important feature, hydrothermal stability tests showed that our materials have a better stability than some siliceous mesoporous materials reported in literature (SBA-15 and MCM-41), this stability was assessed by measuring the decrease in their surface area after steam treatment. For instance, after this hydrothermal test the surface area of $\text{SiO}_2(2:3:20)\text{-E}$ dropped 50%, while that one of SBA-15 and MCM-41 dropped 56% and 90% respectively.

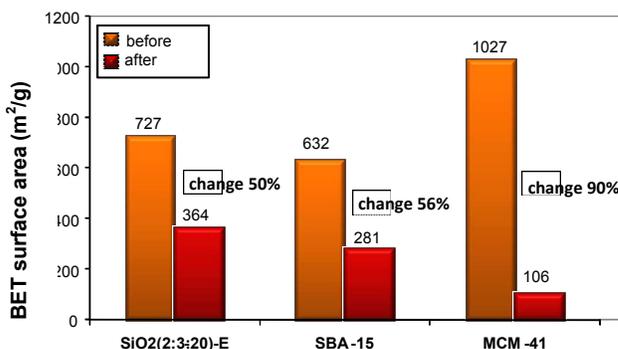


Figure 2. Hydrothermal stability of silica.

4 CONCLUSIONS

Some of the obtained silicas exhibit ideal surface characteristics for a potential application as supports in heterogeneous catalysis. SiO₂(1:1:10)-E and SiO₂(2:1:20)-E are the silicas with the best textural properties, with specific surface area of 824 and 736 m²/g, pore volume of 0,33 and 0.41 cm³/g and pore diameter of 26 and 36.2 Å, respectively. These silicas were synthesized in the presence of ethanol as solvent. Hydrothermal stability tests showed that our materials have a better stability than some siliceous mesoporous materials reported in literature (SBA-15 and MCM-41).

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