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Thermal stability of porous sol-gel phosphosilicates and their surface area stabilisation by lanthanum addition

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Abstract

The thermal stability of porous sol-gel phosphosilicates was studied by comparing the textural features upon calcination between 400 and 550 °C. A significant loss of surface area and pore volume were observed; the first is due to thermal coarsening of the nanoparticles, and the pore volume reduction was ascribed to sintering of the most external nanoparticles producing less void volume. Lanthanum addition was investigated as thermal stabilizer. For the mesoporous phosphosilicate composition, lanthanum addition enhanced the surface area, showing a 45 and 50% improvement with respect to the La-free counterpart; the effect was much less visible for the macroporous composition.

1. Introduction

Porous glasses are an important family of technical materials. They often depend on structural modifications before they are suitable for practical applications (a.o.

production of special glasses, porous SiO_2 in adsorption, catalysis, membranes). Therefore, a great variety of modification procedures is currently available. Such modifications are usually done to improve hydrolytic stability against acid or alkaline solutions, pore size, acidic sites number, surface hydrophobicity and surface polarity, among others [1].

Phosphorus pentoxide is one of the main modifiers for high purity silica materials, extending the application of these composites. Silicate-phosphate properties are attractive in various fields including optics due to UV-radiation sensitivity [2], proton exchange membrane fuel cells [3-6] as well as bioactive glasses in medicine [7-11].

The conventional way of synthesizing phosphosilicates is heating the solid reactants until melting occurs [7,9,11]. This preparation has a series of drawbacks, i.e. energy intensive high temperature and low surface area of the resulting materials [12]. More modern methods, such as sol-gel processes [5,6,10,12-20] do not present such drawbacks, since oxides can be prepared at low temperatures through hydrolysis and polycondensation of the reactants. As a result, melting does not take place, therefore the surface area is not compromised, and less phosphorous is lost in phosphorous oxide volatilization. Other advantages of the sol-gel method include high homogeneity at the molecular level, high purity as well as more control over the substances final surface area and porosity.

One of the key features for the potential application of porous phosphosilicates in adsorption and catalysis, is their thermal stability. The scope of this study is two-fold. The thermal stability of relevant porous phosphosilicates was investigated by comparing the textural changes upon calcination between 400 and 550 °C; two porous phosphosilicates with distinctive meso and macroporosity were studied. Secondly, the addition of La was considered to act as a thermal stabilizer, since it has been a good additive for aluminas [21-24]. The La composition was screened at 2 and 4 wt.% which is

within the typical range reported for aluminas. The La effect was studied in terms of the textural features as obtained by N_2 gas adsorption at -196 °C.

2. Experimental

2.1. Synthesis of the phosphosilicate glasses

The synthesis of the phosphosilicate glasses was carried out based on the work of Aronne et al. [16]. The sol-gel synthesis steps are sketched in Figure S-1 including additional information. Two nominal compositions were investigated, ~17 and ~22 mole.% P as P_2O_5; the materials are denoted as 17PSi and 22 PSi. ICP-OES characterization determined that the final values were 10.5 and 13.3 mole % P_2O_5; these values are much lower than the ones aimed at. This P loss phenomenon was also observed by Aronne et al. [16]; it is attributed to the partial volatilization of P_2O_5 during the calcination.

2.2. Lanthanum impregnation

La(III) was added by wet impregnation using an excess of liquid of an aqueous La(III)-nitrate solution. The La(III)-solution was added at room temperature into the pre-calcined precursor (400 °C, as described in section 2.4), and shaken at room temperature during 5 minutes at 2500 rpm (VWR, digital DVX-2500) to distribute the solution evenly. Afterwards, the solid was dried at 110 °C for 24 h. The resulting material was further calcined at 550 °C as described in section 2.4. The La composition was investigated in two concentrations; 2 and 4 wt.% as La. The La addition step is sketched is Figure S-1 in the overall synthesis protocol.

2.3. Calcination protocol

Calcination was carried out under static air in a LT9/11 Nabertherm box furnace at 400 °C at 1 °C/min for 1h. The resulting material was either: 1) further calcined at 550 °C for 8 h (1 °C/min) or 2) La(III)-impregnated, dried (110 °C, 24 h) and further calcined at 550 °C for 8 h (1 °C/min). These thermal treatments are sketched is Figure S-1 in the overall

synthesis protocol.

An overview of the prepared materials is given in Table S-1. For simplicity, the materials composition is referred as their oxides, i.e. La_2O_3, P_2O_5 and SiO_2. The samples are denoted as 17PSi and 22PSi, followed by the calcination temperature in °C.

2.4. Characterization methods

Nitrogen physisorption analyses were carried out at −196 °C in a Micromeritics ASAP 2420 apparatus. The samples were degassed in vacuum at 250 °C for 10 h. The surface area was calculated using the standard BET method (S_{BET}). The single point pore volume (V_T) was estimated from the amount of gas adsorbed at a relative pressure of 0.98 in the desorption branch. The pore size distributions (PSD) were obtained from the BJH method using the adsorption branch of the isotherms; the mean pore size (Φ_{BJH}) is given by the position of the PSD maximum. The cumulative surface area was calculated based on the NLDFT method.

3. Results and discussion

3.1 Textural features of the starting materials

Two phosphosilicate compositions were investigated with a nominal composition of ~17 and ~22 mole.% P_2O_5. The shape of the N_2 isotherms for these phosphosilicates, calcined at 400 °C, is nearly similar exhibiting parallel and nearly vertical branches (Fig. 1 and 2, bottom). These isotherms are classified of type IV with hysteresis Hl representing solids with high pore size uniformity and facile pore connectivity [25]. Two structural types have been considered within this isotherm; materials that consist of agglomerates or assemblies of spherical particles arranged in a uniform fashion, or materials with cylindrical pore geometry. Since the applied synthesis does not make use of any structural-directing agent, that would allow a geometrical cylindrical assembly, it is believed that the isotherms correspond to agglomerates or spherical nanoparticles that are uniformly arranged.

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Based on the position of the BJH pore size distribution, the 17PSi-based phosphosilicate is purely mesoporous (Fig. 1 top) and the 22PSi-based one is a combined meso- and macroporous structure (Fig. 2 top).

3.2 Thermal stability

The thermal stability was evaluated by comparing the gas adsorption N_2 isotherms, and derived textural parameters, between 400 and 550 °C. Upon calcining at 550 °C, the isotherm of the 17PSi-based phosphosilicate does not change the shape but there are several obvious changes (Fig.1 bottom). The adsorbed gas at p/po below 0.8 is lower than at 400 °C. The inset in Fig. 1 bottom reveals such an effect clearly, which implies a 33% reduction of the BET, from ~87 m²/g (400 °C) to ~58 m²/g (550 °C), Fig. 3. For simplicity, Fig. 3 summarises the absolute and relative changes in surface areas and pore volumes of the studied materials. The monomodal BJH pore size distribution (Fig. 1-top) evidences that the maxima shift from 31.3 nm (400 °C) to 36.7 nm (550 °C); thus the pores expand after applying a higher calcination temperature. This evidences that the BET decrease is originated from the thermal coarsening of the 17PSi glass nanoparticles that gives rise to larger pore sizes. Such an effect is less obvious for the 22PSi-based phosphosilicate (Fig. 2) where the isotherms are nearly identical. The pore size increases subtly from 48.5 to 50.2 nm (Fig. 2, top) and the BET only decreases in 3% (Fig. 3). Therefore, a PSi glass with meso/macropores appears to be more thermally stable, against thermal coarsening, than those purely mesoporous in terms of maintaining the surface area.

Regarding the pore volume, the effect is contrariwise (Fig. 3). The 17PSi-based phosphosilicate does not experience changes in pore volume upon calcining at 550 °C, with respect to 400 °C. The 22PSi-based phosphosilicate reduces the pore volume in 11 %. This is coming from changes in particle sintering that affects the meso/macroporosity,

which is visible in the BJH distribution as a reduction of the maxima intensity (Fig. 2, top).

3.3 Effect of Lanthanum addition

As seen in the previous section, both phosphosilicate compositions are partly unstable; the purely mesoporous 17PSi material losses BET surface area while the meso/macroporous 22PSi material losses pore volume principally.

It is known that La addition stabilizes aluminas [21-24], giving rise to a kinetic retardation of the thermal sintering, by forming lanthanum aluminate on the alumina's surface. We applied a similar approach to these phosphosilicates in two La loadings and their effect was studied on the resulting materials texture.

The La addition did not alter the shape of the isotherms for both phosphosilicates. The isotherm for the La-modified 17PSi550 phosphosilicates was very similar to the La-free counterpart (Fig. 1, bottom). Compared to this La-free material (17PSi550), the BET surface areas were 45 and 50 % higher, for the 2 and 4 wt.% La, which is a remarkable result. This implies that La was effective in stabilizing the 17PSi material against thermal coarsening and this produces a higher surface area. Evaluation of the NLDFT cumulative surface area, for the La-free and La-modified 17PSi-based phosphosilicate materials (Fig. 4), evidences that there is a gain in microporosity but the major gain comes from mesopores up to 30 nm. Thus the effect comes from a lack, or reduced, coarsening between the glass nanoparticles; additional investigation is required to understand the La effect fundamentally, whether it is a similar phenomenon than in aluminas or not.

The pore volume for the 17PSi material did not change much upon calcining at 550 °C and this was also the case for both La-modified counterparts.

In the case of the 22PSi phosphosilicate, the La effect in terms of the surface area was present but less visible with a subtle increase of 7 % for the 2 wt.% and 3% for 4 wt.% La.

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This is not surprising because this material was less affected by calcination; therefore there is less margin for improvement. The pore volume was, on the contrary, most affected with the calcination having 11% reduction from 400 to 550 °C. Lanthanum addition did not improve this effect. At 2 wt.% La the pore volume was subtly enhanced with a 3% increase while at 4 wt.% La this was –2%, than the La-free 500 °C calcined material. Thus La does not play a key role in improving the pore volume.

4. Conclusions

A preliminary thermal stability study of two relevant sol-gel porous phosphosilicates reveals that these structures are thermally unstable. A significant loss of surface area (17PSi composition) and pore volume (22PSi composition) were observed upon increasing the temperature from 400 to 550 °C; due to thermal coarsening of the nanoparticles, while the pore volume reduction was attributed to sintering of the most external nanoparticles.

Lanthanum addition in low concentration by wet impregnation of the 400 °C materials, before preceding to the final 550 °C calcination step, increases the surface area with an enhancement ranging 3 to 50%, while it does not work for the total pore volume. The La effect appears to work preferentially best on purely mesoporous phosphosilicate materials on improving the surface area.

5. Acknowledgements

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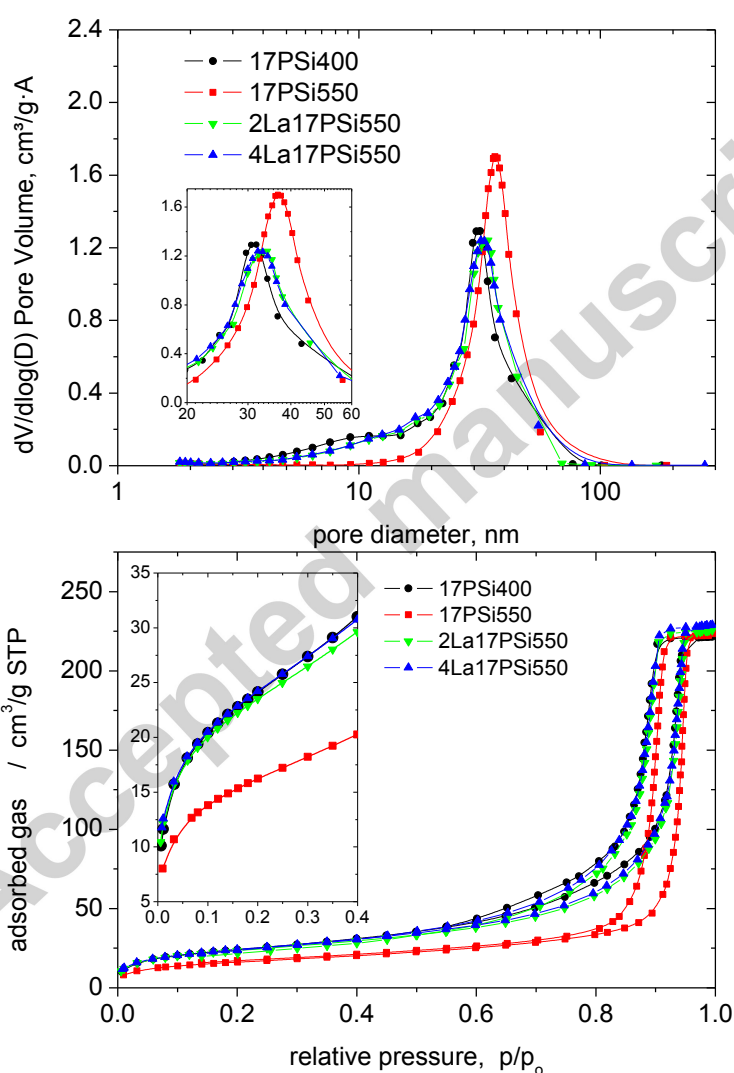
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Figure 1. Bottom) Nitrogen sorption isotherms at −196 °C for the 17PSi-based phosphosilicates (inset: amplification in the p/po range between 0 and 0.4); Top) corresponding BJH pore size distribution. Inset represents a magnification between 20 and 60 nm.
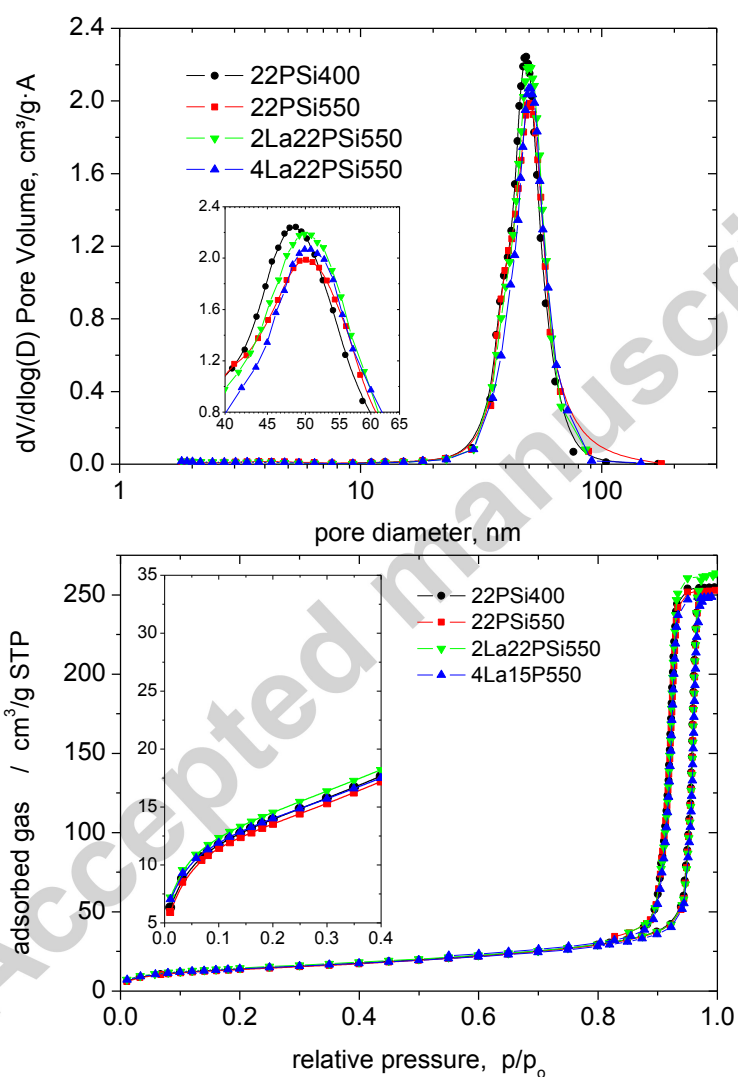
Figure 2. Bottom) Nitrogen sorption isotherms at −196 °C for the 22PSi-based phosphosilicates (inset: amplification in the p/po range between 0 and 0.4); Top) corresponding BJH pore size distribution. Inset represents a magnification between 40 and 65 nm.
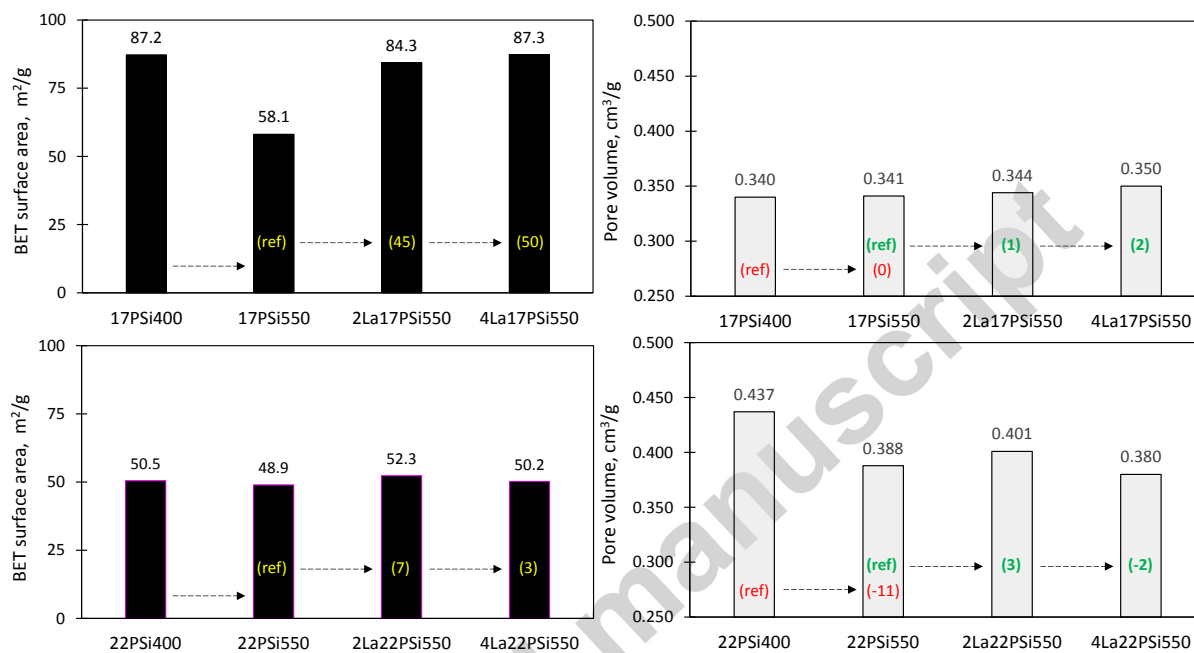
Figure 3. Left) Representation of the BET surface area (S$_{BET}$) and Right) pore volume (V$_T$) for the 17PSi- (top) and 22PSi-based phosphosilicates (bottom). Values between brackets represent the percentage of reduction/increase of the surface area or pore volume with respect to the La-free 400 °C (reference sample discussed in Section 3.2) or La-free 550 °C (discussed in Section 3.3), indicated as ref. Absolute values are represented in the graphs for simplicity, while the raw data are compiled in Table S-2. A larger version of this graph is available in the ESI.
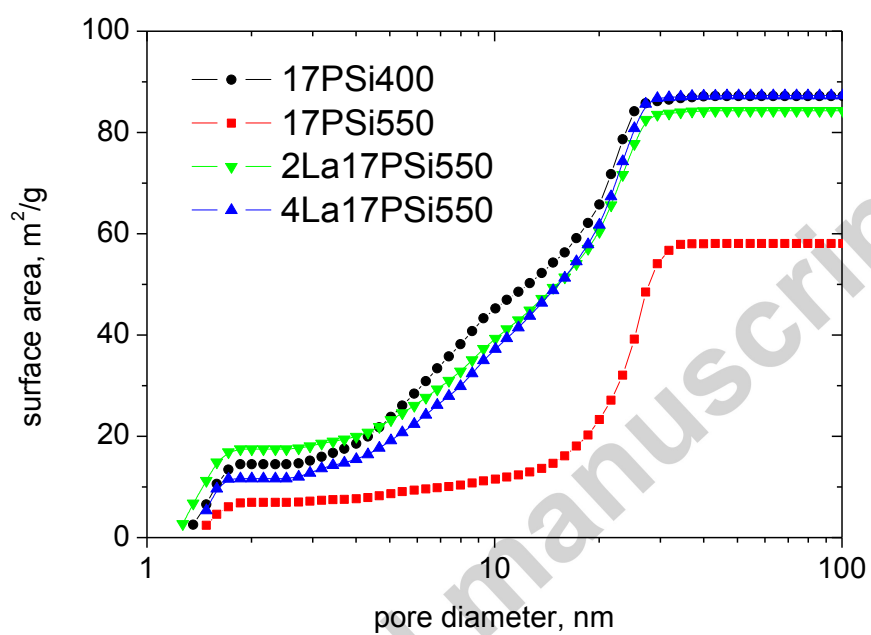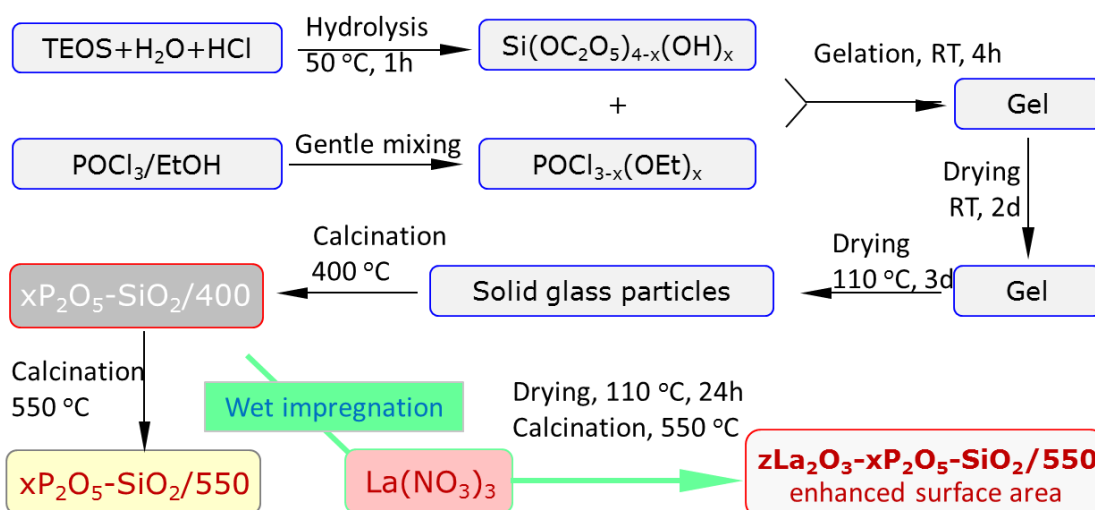
Figure 4. NLDFT cumulative surface area for the La-free and La-modified 17PSi-based

phosphosilicate materials.

Graphical abstract

Highlights

- Relevant sol-gel porous phosphosilicates were found to be thermally unstable.

- Loss of surface area was ascribed to thermal coarsening.

- Pore volume reduction was attributed to sintering of external nanoparticles.

- Lanthanum addition enhances the surface area from 3 to 50%.

- Lanthanum addition does not work for the total pore volume.