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O2 TRAPPING IN SILICA NANO–STRUCTURES WITH HIGH SPECIFIC SURFACES

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Abstract

We report an experimental investigation regarding the entrapping of O_2 molecules inside various silica nano–structured systems having specific surfaces from 50 to 1000 m^2/g. By recording Raman spectra and Near Infrared O_2 emission we studied the O_2 content per mass unit. Our data show that the internal voids of these nanostructured systems can trap O_2 molecules diffusing from the surrounding air or from a pure O_2 atmosphere, whereas the concentration of O_2 that can be trapped in the silica near–surface layer is at least one order of magnitude lower. This low ability is consistently observed in non–porous and porous silica nanoparticles and in mesoporous silica systems. Furthermore, we observed that the O_2 emission appears in the measurements recorded for mesoporous systems as the MCM41 after thermal treatment at 1000 °C when the mesoporous structure collapses, as proved by the variations of the Raman spectra. Considering the high variability in structure and morphology of the ensemble of investigated samples we suggest that the fact that the thin near–surface layer of silica has a low ability in trapping O_2 molecules is a general property of the silica high specific surface systems.

Keywords: oxygen, photoluminescence, nanosilica, Raman spectroscopy

1. INTRODUCTION

The use of amorphous SiO_2 (a–SiO_2 or silica) based materials has been recently extended to nano–structured systems [1–4]. Such materials have various modern applications [4–6] because of the chemical and physical properties of silica [7] and also for their high values of specific surface [3, 4, 7]. Recent investigations illustrated the possibility to obtain Near Infrared (NIR) luminescent SiO_2 based materials by the entrapping of O_2 molecules [8–10]. In details, using laser excitation at about 1064 nm the O_2 molecules trapped inside silica matrix exhibit a luminescence peak at about 1272 nm [8–10], this emission being associated to the transition occurring from the first excited singlet state to the ground triplet state [11]. At variance to common bulk systems, this luminescence could be present before any treatment and can be easily increased in silica nanoparticles by keeping the samples for few hours in pure O_2 atmosphere at temperatures in the range 100–200 °C, since the diffusion time is reduced by the nanosize of the materials [10]. Regarding the silica nanoparticles, it was proposed that they can be described as a shell system [9, 12, 13]. In this model the interior part, named core, has structural properties similar to the bulk systems [12,13]; whereas the exterior part, named surface shell, has a thickness of about 1 nm regardless of the particles dimensions and it has structural properties different from the bulk [12,13]. Recently, it was shown that the ratio between the amplitude of the emission band of the O_2 molecules trapped inside the nanoparticles, and the 800 cm^{-1} Raman band, associated to intrinsic silica vibrational modes [13], decreases with increasing of the specific surface [9]. This finding was interpreted using the shell model, but it was not possible to clarify if O_2 is present in the surface shell and its emission is quenched or if the O_2 is absent in the surface shell. A successive investigation based on the Raman signal of the O_2 showed that the differences in the emission amplitudes are real differences in O_2 concentrations [14]. These two studies [9, 14] highlighted that in comparison with the core the surface shell has a low ability to trap O_2 molecules. In the present manuscript we investigate the ability of thin layers of silica to trap O_2 extending the previous studies to the porous and the mesoporous materials.

2. EXPERIMENTAL

We studied different commercial materials. The fumed silica nanoparticles were produced by Evonik Industries [15, 16]. These materials were synthesized by $SiCl_4$ oxidation in an O_2/H_2 flame at 1100–1400 °C. The starting powders of nanoparticles were pressed in an uniaxial mechanical press at about 0.3 GPa to obtain tablets. The specific surface (S) and the particles average diameter (AD) were estimated by BET method and transmission electron microscopy measurements respectively [15, 16]. It is important to note that the Raman spectra recorded for the tablets coincide with those recorded on the same sample in the form of powders. The only difference is an enhancement of the signal. In the following of the manuscript the fumed silica nanoparticles are named AEOX50 (S=(50±15) m^2/g; AD= 40 nm), AE90 (S=(90±15) m^2/g; AD=20 nm), AE150 (S=(150±15) m^2/g; AD=14 nm), AE200 (S=(200±25) m^2/g; AD=12 nm), AE300 (S=(300±30) m^2/g; AD=7 nm) and AE380 (S=(380±30) m^2/g; AD=7 nm) [15,16]. In addition, we studied one type of porous nanoparticles and four types of mesoporous materials acquired from the Sigma Aldrich [17]. The porous nanoparticles named SiP640 have specific surface in the range 590–690 m^2/g and diameter in the range 5–15 nm [17]. The starting powders were pressed in an uniaxial mechanical press at about 0.3 GPa to obtain tablets. After such operation the Raman spectra do not change significantly. The investigated mesoporous materials are MCM41, HMS, MSU–H and MSU–F samples. The MCM41 has a unit cell of 4.5–4.8 nm, pore size of 2.1–2.7 nm and specific surface of about 1000 m^2/g [17]. The HMS has particles size of ~3 μm, pore diameter of ~3.9 nm and specific surface of ~910 m^2/g [17]. The MSU–H has unit cell of ~11.6 nm, pore size of ~ 7.1 nm and specific surface ~750 m^2/g [17]. The MSU–F has unit cell of ~22 nm, cell window of ~15 nm and specific surface ~562 m^2/g [17]. For the four mesoporous materials we investigated the starting powders since in agreement with previous reported data [18, 19] the production of tablet with high pressure values induces structural modifications.

Raman spectra were recorded at room temperature by using a Bruker RAMII Fourier Transform Raman spectrometer equipped with a 500 mW Nd:YAG laser at 1064 nm. The applied experimental conditions lead to a spectral resolution of 5 cm^{-1} or of 15 cm^{-1}. The samples were kept in pure O_2 atmosphere (60–70 bar) at temperature in the range 100–130 °C, this procedure being named loading in the following.

3. RESULTS

All the Raman spectra reported in the following have been normalized to the signal recorded at 800 cm^{-1}. This normalization procedure was applied since this band is the one that changes the least in shape in the spectra of the different materials, since it is almost independent from the density of silica [20] and because it is representative of the amount of the Si–O–Si linkages being related to the symmetric stretching of the Si–O bond [20]. The Raman spectra of the non porous nanoparticles are reported in **Fig. 1** (panels a–f), in addition to the 800 cm^{-1} band in these spectra we observe all the bands associated to silica. In detail, we observe the R band (peaked at 440 cm^{-1} in the bulk), mainly associated to the oxygen bending vibration in the Si–O–Si linkages [20], the D1 (peaked at 495 cm^{-1}) and D2 (peaked at 605 cm^{-1}) bands related to the four and three member rings respectively and the 1065 and 1200 cm^{-1} bands related to TO and LO modes of the Si–O–Si linkages [20]. As highlighted in a previous investigation [13] the shape of the Raman spectra of these materials depends on the nanoparticles. Furthermore, we detected the presence of other two bands: the first is peaked at about 980 cm^{-1} and is related to the OH vibration in the SiOH groups [21, 22], whereas the second is peaked at about 1538 cm^{-1} and it is related to the emission of O_2 molecules present in the interstices of the silica matrix [8–10]. In panel g of **Fig. 1** we report the Raman spectrum of the porous nanoparticles named SiP640. In this spectrum we note an intense band at 980 cm^{-1} and the presence of a band peaked at 488 cm^{-1} comparable to the so called D0 [23]. It is important to note that such spectroscopic features have been observed in other porous silica materials [23]. Furthermore, we note the absence of the O_2 emission band and of the D2 band and the presence of a Raman band at about 1630 cm^{-1} that can be attributed to the water molecules physisorbed on the silica surfaces [24, 25].

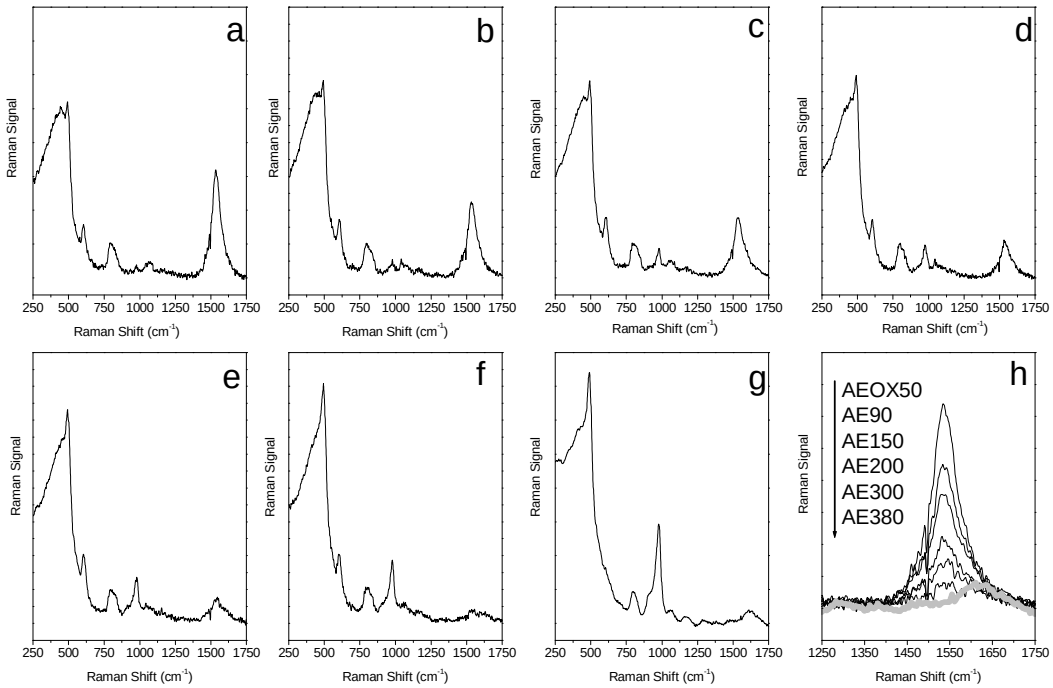

Fig. 1 Raman spectra of the unloaded AEOX50 (panel a), AE90 (panel b), AE150 (panel c), AE200 (panel d), AE300 (panel e), AE380 (panel f), SiP640 (panel g) and zoom of the spectral range 1250–1750 cm^{-1} (panel h) where the O_2 emission is detected, the grey line represents the spectrum of the SiP640

In **Fig. 2**, we report the Raman spectra recorded for the mesoporous systems. Even if the specific features of the spectra depend on the material, in the spectra of the MCM41, the HMS and the MSU–H samples (panels b,c,d) we observe all the bands typically found in silica, whereas in the spectrum of the MSU–F (panel a) the D2 band is absent. In all the spectra of **Fig. 2** we note also the presence of a narrow peak at ~1556 cm^{-1}. This feature is attributable to the Raman Q band of the O_2 present in air [26], furthermore we remark that the Raman band related to the stretching vibration is observed at ~1549 cm^{-1} for the interstitial oxygen molecules in a–SiO_2 [26]. By contrast, the emission of interstitial O_2 is absent in the spectra of the MCM41, HMS and MSU–H materials and if present is near to the detection limit in the MSU–F. Finally, we note that in all the spectra the Raman signal at about 1100 cm^{-1} is higher than the one normally observed in nanoparticles (see **Fig. 1**) or bulk silica [13, 20]. We performed the loading of all samples to study the O_2 molecules trapping inside the silica interstices. As previously reported [9, 10] it is possible to enhance the O_2 content of non porous nanoparticles. In these samples, fixing the temperature and the pressure for each sample the O_2 emission reaches a maximum value as a function of the time [9, 10]. By studying the as–received nanoparticles and the loaded ones (pressure ~75 bar and temperature in the range 100–130 °C) it is found that the ratio between the O_2 emissions of different samples and the one of the AEOX50 is constant before and after the loading [9]. As concerns the other samples the loading increased the O_2 emission just in the MSU–F sample. **Fig. 3a** illustrates the spectra of the AEOX50, of the AE380 and of the MSU–F after loading at ~70 bar and 100 °C. We note that the O_2 emission measured in the AE380 is about one order of magnitude lower than the one measured in the AEOX50, this finding being comparable with the results obtained for the non–loaded samples [9]. Furthermore, we note that in the MSU–F the O_2 emission is slightly lower than the one observed in the AE380. We remark that after about one week from the loading the O_2 emission detected in the MSU–F is about one half with respect to the initial one. Finally, considering the spectra reported in the inset of **Fig. 3a** we can suggest that the loading procedure did not change the Raman spectrum of the MSU–F material. In **Fig. 3b** we report the spectra recorded for the MCM41 and the HMS samples after a thermal treatment at 1000 ° C in air for 5 h. We note that the treatment induced relevant

modifications in both materials, in fact, in their spectra the silica bands changed, the SiOH band disappeared and at 1538 cm^{-1} we detected the emission of O_2 molecules trapped within silica matrix.

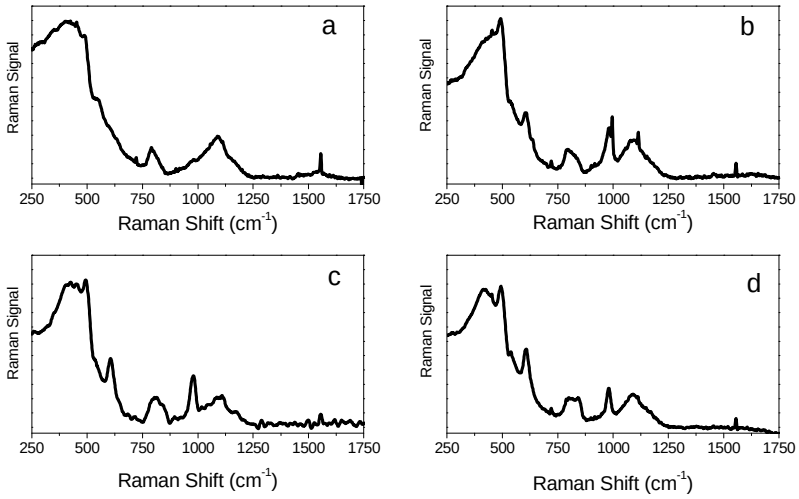

Fig. 2 Raman spectra of the unloaded MSU–F (panel a), MSU–H (panel b), HMS (panel c) and MCM41 (panel d) samples

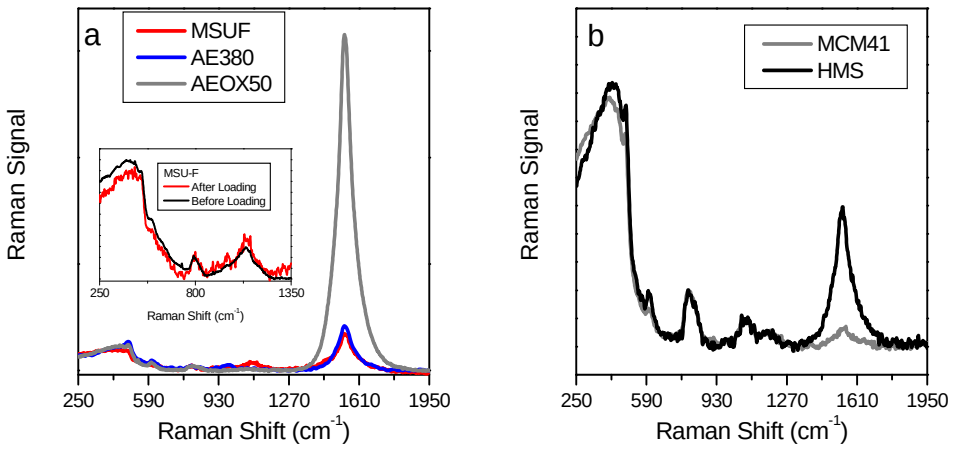

Fig. 3 Panel a, Raman spectra of the MSU–F, AE380 and AEOX50 after loading at about 70 bar at 100 °C; inset, zoom of the spectral range 250–1350 cm^{-1} where the silica intrinsic Raman bands are detected. Panel b, Raman spectra of the HMS and MCM41 samples after thermal treatment at 1000 °C in air for 5 h

4. DISCUSSION

The Raman and O_2 emission measurements have illustrated that in comparison with the other investigated system the non porous nanoparticles contain a relevant quantity of interstitial O_2. The normalization for the 800 cm^{-1} Raman band enables the comparison among the O_2 signals of different materials and, since the 800 cm^{-1} amplitude depends on the silica mass, such comparison is essentially in mass units. First of all, it is important to note that the O_2 emission recorded in the non–loaded nanoparticles is stable on a time scale of years; furthermore, in a totally outgassed AEOX50 sample the O_2 emission comes back to the value reported in **Fig. 1a** after two years, so that one can consider the ratios O_2 emission/800 cm^{-1} reported in **Fig. 1** as the

equilibrium ones. In this case one should expect similar contents of O_2 for mass units. Furthermore, the ratio between the O_2 emission of the different nanoparticles is almost unchanged by the loading procedure.

By using a shell model [9, 12, 13] we can explain the data recorded for the non–loaded and the loaded non–porous nanoparticles with the following scheme: the emission signal is essentially due to the O_2 molecules inside the core of the nanoparticles, whereas the contribution from the surface shell, having a thickness of about 1 nm, is at least one order of magnitude lower [9, 14]. This variability in emission amplitude is due to a real difference in concentrations of entrapped O_2 molecules since a similar trend was observed studying the Raman signal of the O_2 inside the silica interstices [14]. It is also found that increasing the specific surface, in the porous and in the mesoporous materials, one observes that the O_2 is absent or near to the detection limit in the not loaded MSU–F and that the O_2 loading procedure is ineffective or poorly efficient in these materials. These findings support the suggestion that a near surface thin layer of silica has a low ability to trap O_2 molecules. In this context, considering the SiP640 we note that for reaching a specific surface of 640 m^2/g with a single pore concentric with a particle with diameter of 10 nm, the radius of such pore has to be 3.5 nm. In this schematic case we have a hollow sphere having a wall of thickness of 1.5 nm so that even at the center of the wall the distance from the surface is 0.75 nm which is lower than 1 nm. Even if these nanoparticles contain many pores with smaller radii the above considerations can give an idea on the empty and the filled volumes in the SiP640 materials The presence of the O_2 emission in the Raman spectra of the thermally treated MCM41 and HMS and the deep modifications induced by the thermal treatment on the spectral features of the Raman activities of these two materials can be interpreted as follows: the absence of the SiOH Raman band can be considered the result of the thermally induced reaction SiOH+HOSi → Si–O–Si [25]. Considering that in these two materials such groups are on the surfaces, because of their high specific surface [25], the collapse of the pore can be suggested and as a consequence of this latter and because of the high temperature the O_2 present in the ambient atmosphere can diffuse inside the matrix where it remains trapped at room temperature. Finally, we note that the low ability to trap O_2 of a thin near surface layer of silica is observed in samples with different morphologies, structures and in samples as the MSU–F with undetectable SiOH content. Basing on this observation we can reasonably suggest that such low ability, in comparison with the core of the nanoparticles, is a general feature of this type of systems.

5. CONCLUSION

We investigated different types of silica nanostructured systems having specific surface ranging from 50 to 1000 m^2/g, the materials differing for structure and morphology; in fact, the ensemble of the samples contains nanoparticles, porous nanoparticles and four mesoporous materials. All the recorded data suggest that a near surface thin layer of silica has a low ability, per mass units, of trapping O_2 molecules.

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