

Nanoparticulated ceria dispersed over silica: XPS study of the redox deactivation process

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Abstract

Cerium oxide is widely employed in many technological applications. Despite cerium is relatively abundant in the earth crust, its ores are quite scarce, and limited to few countries in the world. This fact, together with the more and more extended applications of ceria, its prices have increased in the past years. Finding ways to decrease ceria content, maintaining good properties is a main goal in many recent studies about ceria. One of the most important applications for ceria and ceria-based oxides, concerns their use as catalysts and catalytic supports [1]. It is well known that ceria redox properties can be modulated by changing its particle size. Dispersion of ceria on a proper support can be used to decrease ceria content of the catalysts keeping or even improving its redox properties. In this work, we have dispersed small ceria nanoparticles over porous silica nanoparticles. Redox behaviour of this material, as well as its stability when submitted to high temperature treatments has been studied.

Porous silica nanoparticles (average diameter 40 nm) were used to prepare two different samples by chemical precipitation of cerium (III) nitrate using HMT [2]. Sample CS-1 was prepared by this method, with a Ce/Si molar ratio of 0.23. For sample CS-2 an anionic surfactant (SDBS, Sodium Dodecyl Benzene Sulfonate) was also added, and its Ce/Si molar ratio was set to 0.39.

TPR-MS studies were performed in an experimental device coupled to a Thermostat GSD301T1, quadrupole mass spectrometer from Pfeiffer, using a 5% H₂/Ar flow. Electron Microscopy studies were performed in a JEOL2010F TEM/STEM microscope. The electron microscopy sample grid was prepared by depositing the sample powder directly onto holey-carbon Cu grids.

A self-supported wafer of the ceria-silica sample was successively subjected to a series of reducing and oxidizing treatments, and investigated by XPS on a Kratos Axis Ultra DLD instrument equipped with a catalytic cell allowing a clean transfer of the pretreated samples to the analytical chamber. Spectra were recorded with monochromatized AlK α radiation (1486.6 eV). Surface charging effects were compensated by using the Kratos coaxial neutralization system. The binding energy (BE) scale was calibrated with respect to the C 1s signal at 284.8 eV. Spectral processing was performed with CasaXPS software.

The electron microscopy study of the ceria-silica samples (not shown) indicates that ceria is well dispersed on the porous silica as nanoparticles with an average size of about 1-1.5 nm, both on the external surface of the silica as well as inside the pore structure.

The redox behaviour of the samples was studied by TPR. Fig. 1 shows the reduction profile for CS-1, CS-2 and a pure ceria sample. A first TPR performed on the CS-1 and CS-2 samples (thick lines), shows that for both samples the reducibility is significantly enhanced with respect to pure ceria. After this TPR experiments, the ceria-silica samples were reoxidized and then submitted to a new TPR experiment (thin lines in Fig.1). This second TPR shows a strong deactivation of the ceria-silica samples, as there is a strong reduction in the TPR for CS-1, and a complete disappearance of the TPR signal for CS-2.

XPS studies were performed on the samples, after being submitted to successive reduction and reoxidation treatments. After each treatment, surface Ce(III) content was measured. Due to the small size of ceria nanocrystals, XPS data is representative of the behaviour of all ceria contained in the samples. For sample CS-1, Fig. 2 shows Ce(III) evolution throughout the successive reduction at temperatures ranging from 350 to 900°C. After each reduction %Ce(III) was measured by XPS, then the sample was reoxidized at 350°C, and the %Ce(III) measured again. Fig. 2 shows how Ce reduction degree increases when increasing reduction temperature, reaching 100% reduction after reduction treatment at 700 and 900°C. The amount of remaining Ce(III) after reoxidation treatment at 350°C increases gradually after each reduction/reoxidation cycle, being as high as 86% after the redox cycle at 900°C. A further reoxidation at 600°C is only able to decrease remaining Ce(III) to 76%, but complete recovery of Ce(IV) could be reached after reoxidizing at 800°C.

In the case of CS-2 sample, a similar behaviour was observed, remaining all cerium as Ce(III) after reduction at 900°C and reoxidation at 350°C, in well agreement with the second TPR in Fig. 1.

In conclusion, two ceria-silica samples, with highly dispersed ceria, were prepared. Both samples exhibit better reducibility than bulk ceria. However, thermal deactivation was observed, as a blockage of cerium

in the trivalent state. This deactivation proceeds gradually as reduction temperature is increased, and can be reverted by reoxidation at high temperature.

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References

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Figures

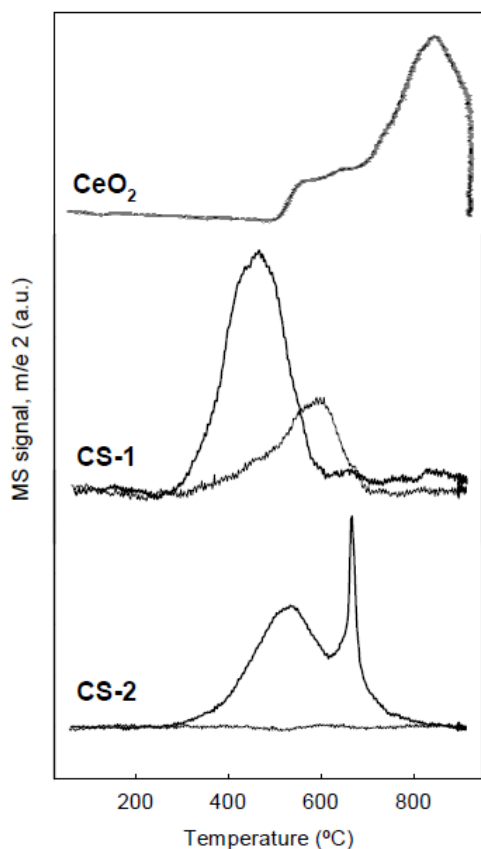


Figure 1. TPR-MS for the reduction under H₂/Ar of the ceria-silica samples. The thick line corresponds to a first TPR experiment, and the thin line to the second TPR. The reduction profile for a ceria massive oxide is included for comparison.

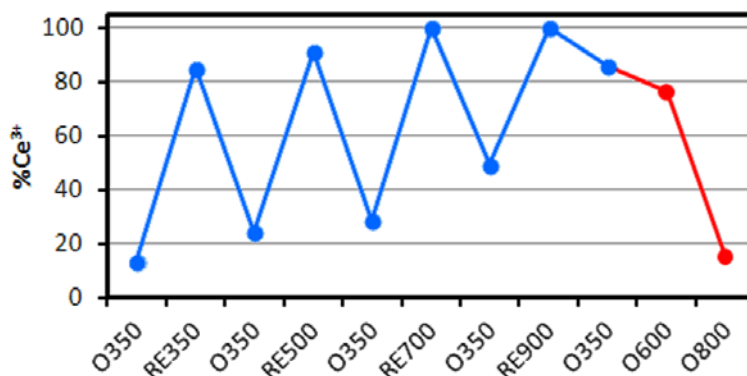


Figure 2. Ce(III) percentage measured by XPS for sample CS-1 submitted to the oxidizing and reducing treatments indicated in the figure.