

Determination of the Cerium Oxidation State Incorporated into MCM-41 Silica Matrix by HR-STEM Imaging and EELS Spectra

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Given the current trend for the synthesis of novel 2-dimensional materials to technological and scientific applications, nowadays there is a growing interest to determine the structural and chemical properties of the species a nanometric scale. In the present research we concentrate on the determination of cerium oxidation state isomorphically incorporated into high ordered MCM-41 mesoporous silica to determine its multi-point structural variation. A series of novel Ce-doped MCM-41 catalysts was prepared by varying the Ce loading from 2.9 wt% to 13.2 wt% via hydrothermal method using CTAB as surfactant. The hybrid composites were characterized by high angle annular dark field (HAADF) imaging and spatially resolved electron energy-loss spectroscopy (EELS) employing a scanning transmission electron microscope (STEM). The $M_{4,5}$ energy edges for the Ce in the form of spectrum images (SI) were obtained. First, an elemental characterization of the nonstoichiometric ceria-silicas was done from a clear observation of Ce $M_{4,5}$ peaks (883, 901 eV) and the single Si K peak (1839 eV). The analyzes of the energy-loss near-edge structure (ELNES) of the pair Ce $M_{4,5}$ peaks provided qualitative information about the Ce^{4+}/Ce^{3+} oxidation states of cerium species incorporated into the walls of the mesoporous silica. A previous characterization with the X-ray photoelectron spectroscopy (XPS) technique was done to all oxygen-deficient Ce-MCM-41 materials in order to discard electron beam damage in the STEM-EELS analysis. The STEM-EELS spectrum imaging provides a facile method to qualitatively identify the cerium oxidation state grafted in the Si-O-Si framework of mesoporous silica. The analytical results here presented shown that the Ce^{3+} cation is present in all functional materials as was indicated by the shift of the pair Ce $M_{4,5}$ peaks to a lower binding energy and the increase of the M_{5}/M_{4} ratio. The cerium ions were found to change from Ce^{4+} to Ce^{3+} owing to oxygen deficiency near to the surface of all nanoparticles. In summary, the Ce $M_{4,5}$ -edge EELS spectra have been used to evaluate the structural variation of cubic CeO_2 to an oxygen deficient Ce_2O_3 structure incorporated into MCM-41 silica.

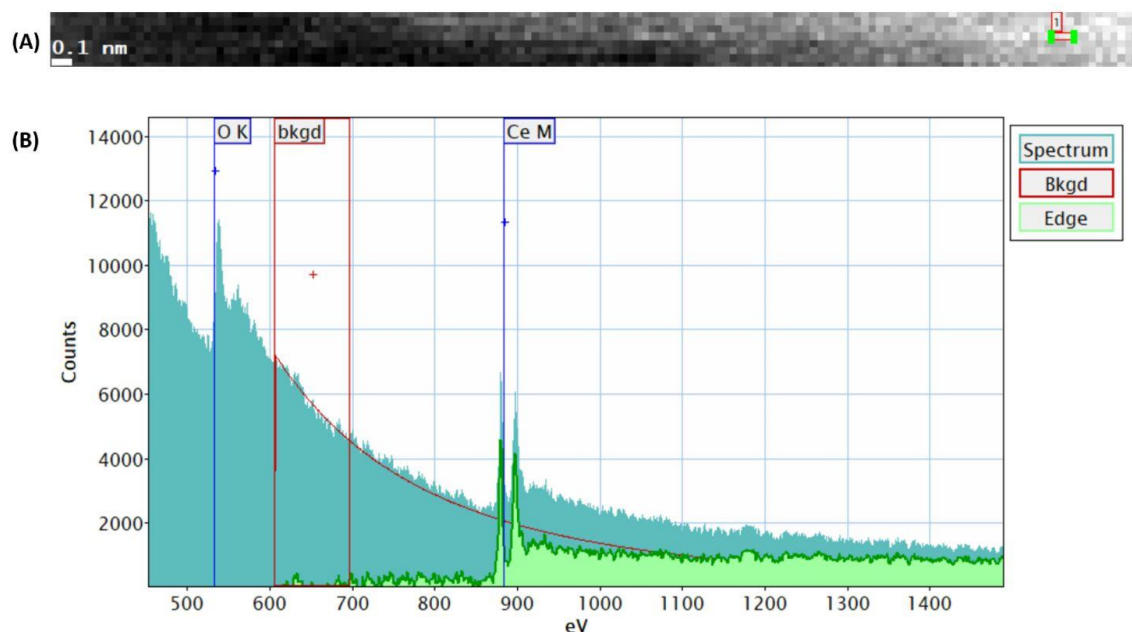


Figure 1. (A) spectrum image (SI), (B) EEL spectrum extracted from SI depicting oxygen K-edge, cerium M4,5 edge, background integration window and cerium signal (green) with background subtraction.

References

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Borja-Urby, R., Paredes-Carrera, S. P., Viltres-Cobas, H., Santiago-Jacinto, P., Paraguay-Delgado, F., Herrera-Pérez, G., ... Morales-Cruz, D. (2019). Confined volume plasmon spatial distribution by low-loss EELS on self-assemble bismuth nanoparticles. *Journal of Electron Spectroscopy and Related Phenomena*, 237.

<https://doi.org/10.1016/j.elspec.2019.146891>