

In Situ Time-Resolved Synchrotron Powder X-ray Diffraction: Reduction of Cerium Oxide

J. Hanson, J. Kim, J. Rodriguez (BNL), P. Lee (ANL), P. Chupas and C. Grey (SUNY, SB)

Beamline(s): X7B

Introduction: The reduction of metal oxides by hydrogen is frequently employed to prepare active catalysts. Synchrotron-based time-resolved X-ray diffraction (XRD), X-ray absorption fine structure (NEXAFS/EXAFS), photo emission, and first-principles density-functional slab calculations were used to study the reaction of H₂ on NiO. The transformation of NiO to Ni takes place after an induction period without any intermediate phases. The interaction of H₂ with NiO surface is shown to be much stronger at oxygen defects. The induction period is consistent with the slow formation of oxygen defects at the beginning of the reduction [1]. Measurements of the reduction of α -NiMoO₄ and β -CoMoO₄ by H₂ show important differences in the behavior of these two mixed metal oxides. The reaction of H₂ at elevated temperatures (> 500°C) with α -NiMoO₄ results in nearly amorphous material, while the reduction of β -CoMoO₄ forms the stable intermediate Co₂Mo₃O₈ [2]. It has been shown that the incorporation of H₂ in cerium oxide at elevated temperatures occurs prior to reduction [3]. The partial reduction of has been observed by neutron and X-ray diffraction [4]. We have further investigated these processes with in situ time-resolved XRD.

Methods and Materials: Samples of CeO₂ were loaded in a sapphire capillary attached to a flow-reaction cell similar to those described in refs. [5,6]. The sample was heated in the range of 150-300°C with a small resistance heater wrapped around the capillary. A 5%H₂/95%He mixture was flowed through the capillary and reactant gases were sampled with a SRS RGA. The XRD data were collected with a MAR345 image plate detector and the powder rings were integrated using FIT2D code [7]. The wavelengths were 0.9200Å at X7B NSLS and 0.15358Å at ID1 APS. Refinements of structural features with these data are underway.

Results: Typical effects of temperature and gas composition on cell dimension are show in Fig 1. The cell expansion and product formation were measured simultaneously and the result are shown in Fig 2.

Conclusions: There was an expansion in the unit cell of the reduced particles probably as a consequence of a partial Ce⁴⁺ → Ce³⁺ transformation and the sorption of hydrogen [8].

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References: [1]. J.A. Rodriguez, J. C. Hanson, A. I. Frenkel, J.Y.Kim, and M. Perez, *J. Am. Chem. Soc.* **124**, 354, (2002). [2]. J.A. Rodriguez, J.C. Hanson, J.Y. Kim and J.L.Brito, *Catalysis Letters* **82**,103 (2002). [3]. J.L. G. Fierro, J.Soria, J. Sanz and J. M. Rojo, *J. Solid State Chem.* **66**. 154 (1987). [4]. Ozawa, M. and Loong, C.K., *Cat. Today*,**50**,392 (1999). [5]. Chupas, P. J., Ciralo, M.F., Hanson, J.C. and Grey, C.P., *J. Am. Chem.Soc.*, **123**, 1694 (2001). [6]. Clausen, B. S., Steffensen, G., Fabius,B., Villadsen,J., Freidenhans, R and Topsoe, H, *J. Catal.* **132**, 524 (1991) [7] Hammersley,A. P., Svensson, S.O. and Thompson,A., *Nucl. Instr. Methods Phys.*, **346**, 321 (1994). [8]. Rodriguez, J. A., Hanson, J. C. ,Liu,G, Iglesias-Juez, A. and Fernández-García, M. *J Phys Chem B* (submitted)

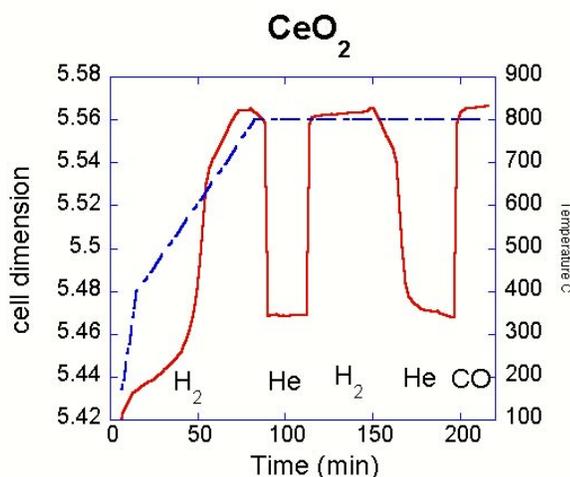
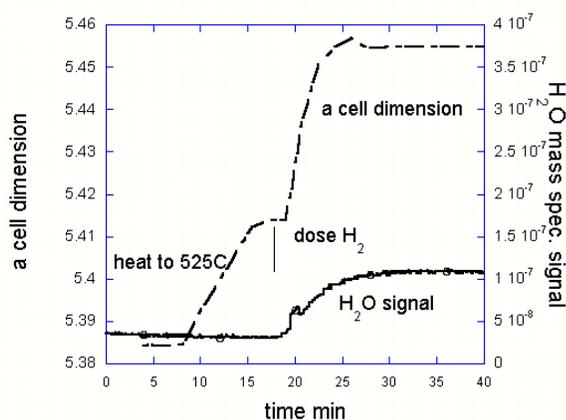


Fig1. Cell expansion under different conditions

Fig. 2. Typical cell expansion and product formation for Zr doped CeO₂