



	Experiment title: Role of CeO2 in Ce-promoted iron oxide catalysts for CO2 utilisation (submission for SNBL (BM01B) through DUBBLE (BM26) CRG collaboration)	Experiment number: 26-01-941
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Report: (max. 2 pages)

Introduction

The aim of the present study was to investigate FeO_x catalysts, either promoted with CeO₂ or CeZrO₂, in order to determine the role of the promoter in the redox behaviour of these FeO_x catalysts. Redox reactions were performed with CO and CO₂ or O₂ and followed on line by MS, while examining the crystalline phases of FeO_x and Ce(Zr)O₂ by in situ XRD and the local structure of Ce by means of XAS.

Experiments performed

In view of optimal XAS signal, a sample of ~40 mg was loaded between with 2 quartz wool plugs into a 3 mm quartz capillary, which fits into the capillary frame setup of SNBL, allowing in situ XAS and XRD. After aligning the sample for combined XAS and XRD, high quality XRD patterns and XAS spectra were obtained. XAS spectra at the Ce K edge yielded EXAFS measurements up to $k = 15 \text{ \AA}^{-1}$ at room temperature (see Fig. 1).

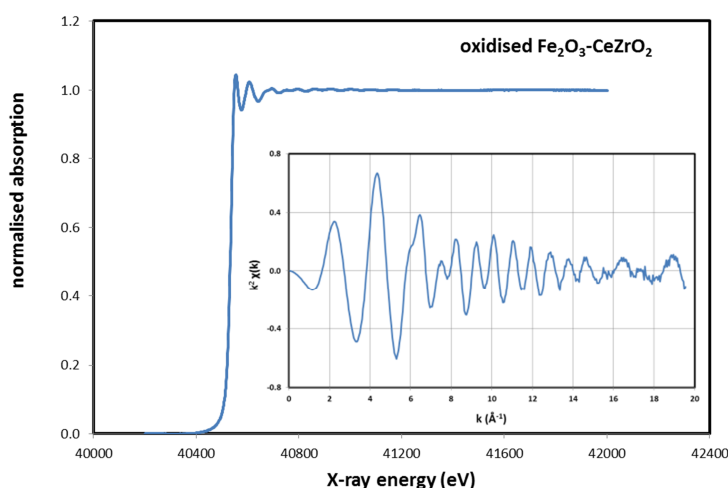


Fig. 1: Ce K edge scan for oxidised Fe₂O₃-CeZrO₂ at 50°C; inset: full EXAFS signal $k^2 \cdot \chi(k)$

Cycling redox measurements were performed on two samples 80wt%FeO_x-20wt%CeO₂ and 80wt%FeO_x-20wt%Ce(Zr)O₂ at 500, 600 and 650°C. The XRD patterns showed clear reduction of the Fe₂O₃, first to Fe₃O₄, then to FeO and even Fe, depending on reducing conditions or times (see Fig. 2). In addition to these phase transitions, the CeO₂ or CeZrO₂ diffractions and peaks from the different FeO_x phases showed changes in peak widths, due to increasing particle size (sintering effect) (see Fig. 3).

The Ce-K edge XAS measurements, on the other hand, show a clear evolution of the oxidation state and structure from the point of view of the Ce cations within the FeO_x-Ce(Zr)O₂ structure, which is complementary to the XRD results.

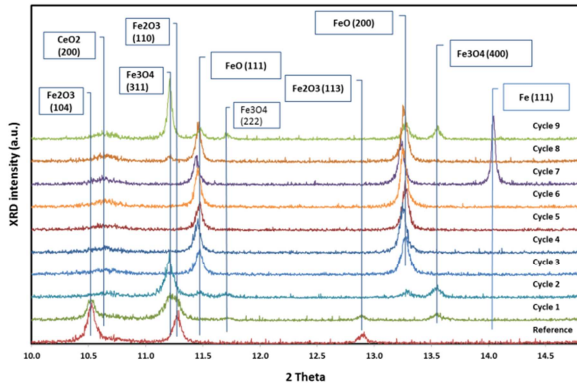


Fig. 2: XRD patterns from $\text{Fe}_2\text{O}_3\text{-CeZrO}_2$ after 5 min CO reduction half-cycles at 600°C , with 5 min CO_2 re-oxidation in between (not displayed) (5% CO/He, 30 ml/min).

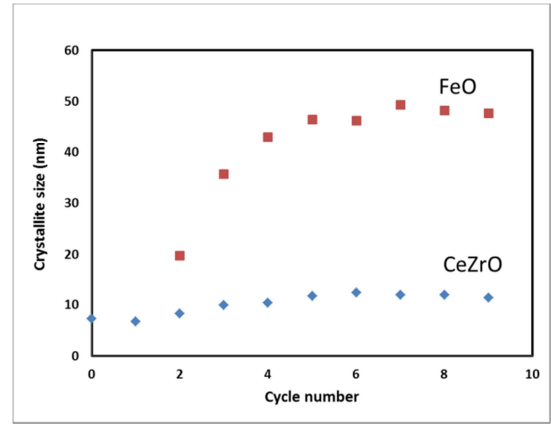


Fig. 3: crystallite size for FeO (after first formation) and CeZrO_2 determined on $\text{Fe}_2\text{O}_3\text{-CeZrO}_2$ during consecutive CO reduction cycles

In Fig 4 the magnitude of the Fourier transformed k^3 -weighted $\chi(k)$ EXAFS signal, i.e. $|\chi(R)| = |\text{FT}\{k^3\chi(k)\}|$, is shown for the $\text{Fe}_2\text{O}_3\text{-CeZrO}_2$ sample at 600°C . The blue line corresponds with a fully oxidized CeZrO_2 state before the redox cycling was started. The red plot represents the $|\chi(R)|$ signal after a deep reduction in the 7th cycle. The first peak amplitude is a measure for the oxygen coordination around the $\text{Ce}^{3+/4+}$ cation, indicating that the oxygen content is significantly higher for the fully oxidized Ce(Zr)O_2 state than for the deeply reduced state. By repeating this inspection of the first peak height in the $|\chi(R)|$ signal for each half cycle, the oxygen content around the $\text{Ce}^{3+/4+}$ cation can be monitored throughout the redox cycles. The result of this procedure is displayed in Fig. 5. An analogous result can be obtained for other temperatures and the other sample $\text{Fe}_2\text{O}_3\text{-CeO}_2$.

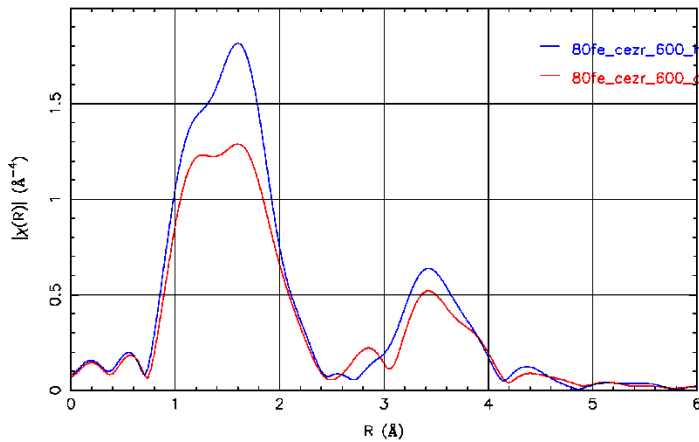


Fig. 4: $|\chi(R)|$ signal for $\text{Fe}_2\text{O}_3\text{-CeZrO}_2$ at 600°C ; (blue) fully oxidized state; (red) deeply reduced state.

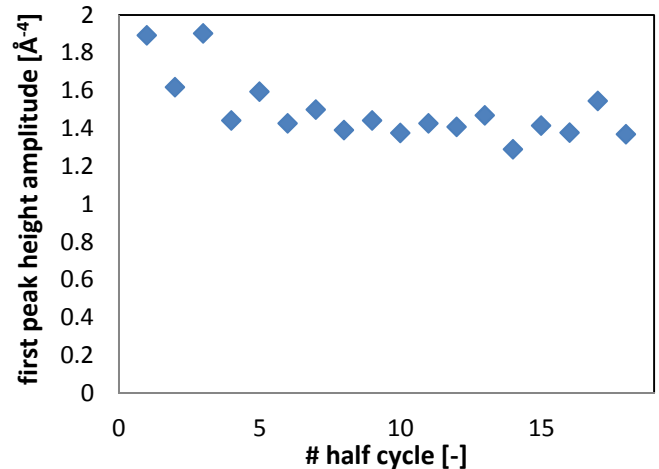


Fig. 5: first peak amplitude after each half cycle of the redox process for the $\text{Fe}_2\text{O}_3\text{-CeZrO}_2$ sample at 600°C .

Finally, in Fig. 6, a comparison is given between the $|\chi(R)|$ signal of the $\text{Fe}_2\text{O}_3\text{-CeZrO}_2$ sample (blue) and the $\text{Fe}_2\text{O}_3\text{-CeO}_2$ sample (red) in oxidized state at 600°C . One can see a larger shoulder in the first peak and a larger amplitude in the second peak for the CeO_2 containing sample with respect to the CeZrO_2 containing sample. This feature is caused by the larger backscattering amplitude of Ce vs. Zr, due to its higher atomic weight (i.e. $\text{Ce/Zr} \approx 1.5$).

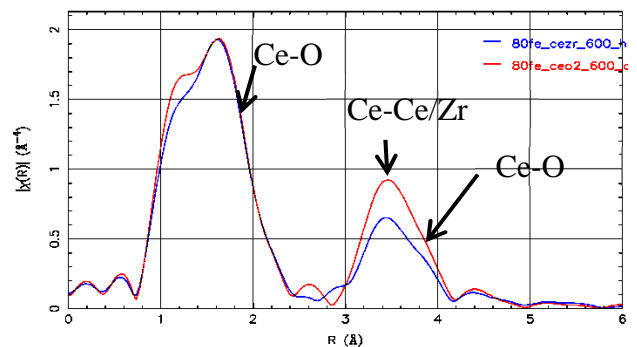


Fig. 6: $\text{Fe}_2\text{O}_3\text{-CeZrO}_2$ (blue) vs $\text{Fe}_2\text{O}_3\text{-CeO}_2$ (red).