

	Experiment title: Redox behavior of modified iron oxide materials for the utilization of CO ₂ studied by in-situ XAS	Experiment number: 26-01-1012
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Shifts: 18	Local contact(s): Alessandro Longo, Dipanjan Banerjee	
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Summary

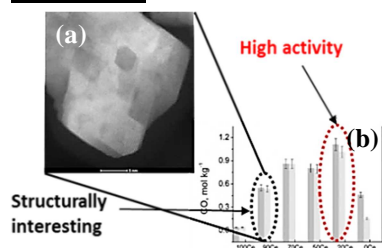


Figure 1: (a) TEM image of 10wt% Fe₂O₃-90wt% CeO₂ showing faceted material; (b) CO produced after the 1st (dark bar) and 10th cycle (light bar); highest activity is observed for 80wt% Fe₂O₃-20wt% CeO₂. [1]

A detailed structural investigation during H₂ temperature programmed reduction (TPR), CO₂ temperature programmed oxidation (TPO) and isothermal cycles (H₂-He-CO₂-He) was performed on Fe₂O₃-CeO₂ materials using *in situ* XAS and XRD. The aim was to understand the role of structural transformation leading to deactivation. Based on our previous study, the structurally most interesting (10wt% Fe₂O₃-CeO₂, TEM) and the catalytically most active material (80wt% Fe₂O₃-CeO₂, activity tests) were investigated (Figure 1), both in as prepared and cycled state. In addition to this, a model Fe₂O₃-CeO₂ material with Fe:Ce = 1:1 mole ratio was equally studied.

Experimental conditions

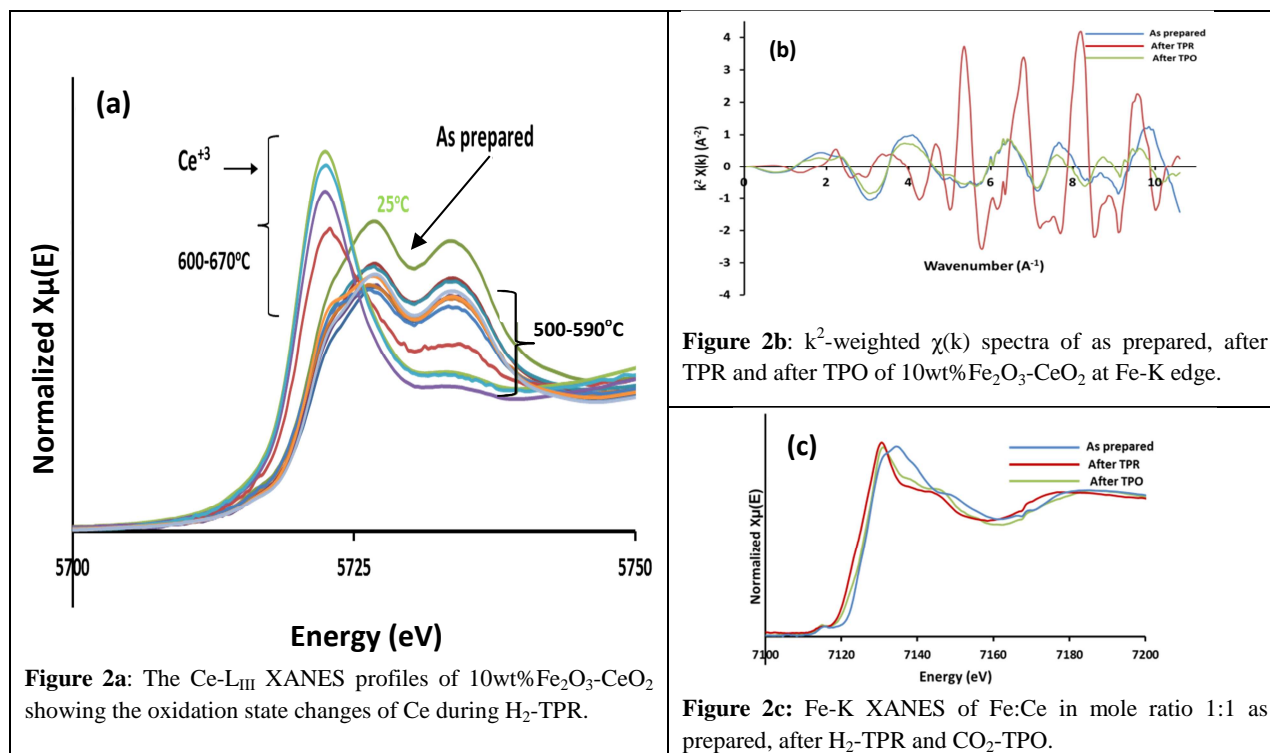
- **H₂-TPR and CO₂-TPO** experiments were performed at a uniform ramp rate of 20°C/min with short XANES measurements (5 min) to a temperature of 700°C with a dwell time of 5 min. Each CO₂-TPO included re-oxidation with air during dwell time, as high-temperature O₂ treatments can induce important structural phase changes which counteract material deactivation. Each treatment was preceded and followed by a room temperature EXAFS scan to study the local structural evolution compared to its fresh/pre-treated state. The study was carried out at both Ce-L_{III} and Fe-K edges in order to obtain complementary structural and chemical information from both Fe and Ce species.
- An **isothermal cycling** study using short XANES measurements (3 min) coupled with *in situ* Mythen XRD was performed at 650°C on material with Fe:Ce in 1:1 mole ratio to study the structural changes during reaction. The XANES were recorded at the Fe-K edge. At the beginning of each XRD scan, a well-performing DUBBLE macro was used to correct 2θ angles for changes induced by shifts in the X-ray energy.

Experiments performed and results

The as prepared materials 10wt% Fe₂O₃-CeO₂, 80wt% Fe₂O₃-CeO₂ and Fe:Ce in mole ratio 1:1 were subjected to subsequent **TPR and TPO** to investigate the **material transformations**.

The changes in Ce-L_{III} XANES white line intensity enable to follow the oxidation state evolution in 10wt% Fe₂O₃-CeO₂ during TPR as seen in Fig. 2a. The final XANES spectra after reduction show the formation of Ce⁺³ state. The information from the full EXAFS scans after each treatment will enable to distinguish the structural differences after the reduction and re-oxidation treatment. The k²-weighted spectra at the Fe-K edge of 10wt% Fe₂O₃-CeO₂ represent the signals of the as prepared, reduced and oxidized state as shown in Fig. 2b. The changes between the reduced state (red curve) and the other

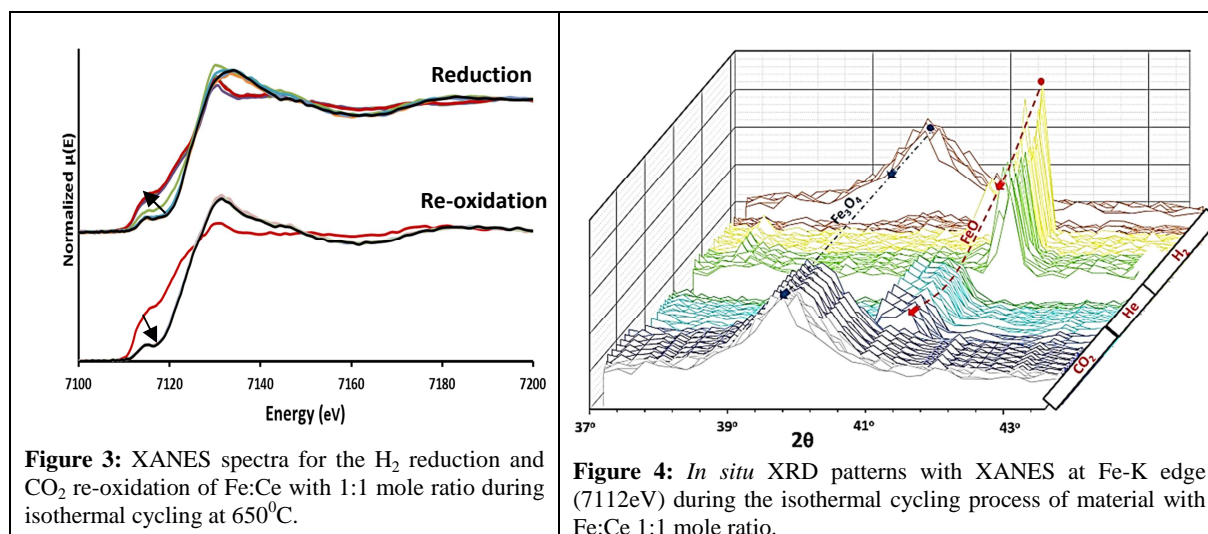
states is quite obvious. A detailed modeling of the EXAFS scan will yield the exact environment of Fe and the structural changes associated.



Similarly, the Fe-K XANES (fluorescence mode) enabled to follow the reduction of iron oxide in the sample with Fe:Ce in mole ratio 1:1. The pre-edge features after TPR and TPO remain the same, indicating the same local environment. However, the edge energy shift towards lower energy indicates reduction (red spectrum in Fig. 2c). Linear combination and detailed EXAFS modeling will yield insight in the reduction and oxidation process.

To study the role of structural transformations during redox cycling, the sample of Fe:Ce in mole ratio of 1:1 was subjected to **isothermal cycles** at 650°C.

The changes in oxidation state were followed by *in situ* XAS and XRD. The Fe-K XANES spectra clearly show the evolution of oxidation state (Fig. 3). During the reduction, the most reduced phase is metallic Fe, while the most oxidized phase resembles Fe₃O₄. The time resolved XRD measurements at Fe-K edge provide a clear insight in the phase changes during reaction (Fig. 4). From the XRD pattern, Fe₃O₄ is reduced to FeO, while the deeper reduction to metallic Fe can be inferred only through XAS.



[1] V.V. Galvita, H. Poelman, V. Bliznuk, C. Detavernier, G.B. Marin, CeO₂-Modified Fe₂O₃ for CO₂ Utilization via Chemical Looping, *Industrial & Engineering Chemistry Research*, 52 (2013) 8416-8426.