

Experiment Report Form

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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Redox pathways and reactivity of Ru and K promoted Fe-Cu based oxygen carriers

Experiment number:
01-01-927

Beamline:
01-01-896

Date of experiment:
from: 23.10.2013 to: 29.10.2013

Date of report:
25.04.2014

Shifts:
15

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Received at ESRF:

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Report:

1. Overview

The main aim of our experiments (SNBL-BM01B beamline, 01-01-896, 23-29 October, 2013) was to probe the redox pathways of (i) ZrO₂-stabilized Fe₂O₃, (ii) Ru doped, ZrO₂-stabilized Fe₂O₃ and (iii) CuO promoted, ZrO₂-stabilized Fe₂O₃ at temperatures relevant for chemical looping combustion (CLC) *i.e.* 750°C. CLC is an emerging technology for the generation of electricity and/or H₂ while inherently capturing CO₂.¹⁻³ The determination of the redox pathways of Fe₂O₃ at typical operating temperatures is an important step towards a better understanding of the CLC process and to accurately determine the kinetic constants of the materials. Recent studies reported in the literature revealed that the presence of promoters, such as K or Ru, increases the reducibility of Fe-Cu-based catalysts.⁴ However, XAS measurements were typically carried out in the temperature range 200-500 °C (*i.e.* temperatures relevant for the Fischer-Tropsch process but not for CLC). Therefore, in this study, we have investigated the reduction and oxidation pathways of ZrO₂ supported, Fe₂O₃ based oxygen carriers using in-situ Fe K-edge XAS at temperatures relevant for CLC (750°C). Additionally, the effect of promoters (Cu or Ru) on the reducibility of the oxygen carriers was assessed.

2. Data collection

The reduction and oxidation reactions of the following materials were studied *in-situ* at 750 °C:

- (a) ZrO₂-supported, Fe₂O₃ containing 30 wt. % Fe₂O₃.
- (b) ZrO₂-supported, Fe₂O₃-based doped with 0.5 wt. % Ru (30 wt. % Fe₂O₃).
- (c) ZrO₂-supported, Fe₂O₃-based (30 wt. % Fe₂O₃) promoted with 10 wt.% CuO.

All oxygen carriers were reduced using a gas mixture containing 5 vol. % H₂ in He (25 mL/min). The oxidation reaction was performed using 5 vol. % O₂ in He (25 mL/min). The oxygen carriers were placed in a quartz capillary reactor of 1 mm outer diameter and heated via an air blower. The gas flow rates were controlled via mass-flow controllers.

3. Results

Fe K-edge XANES spectra of unpromoted, CuO promoted and Ru doped Fe₂O₃ (supported on ZrO₂) in their oxidized and reduced forms are shown, respectively, in Figure 1(a) and (b). The oxidized and reduced XANES spectra of the three different oxygen carriers are similar to the XANES spectra of the reference materials Fe₂O₃ and Fe acquired at room temperature.

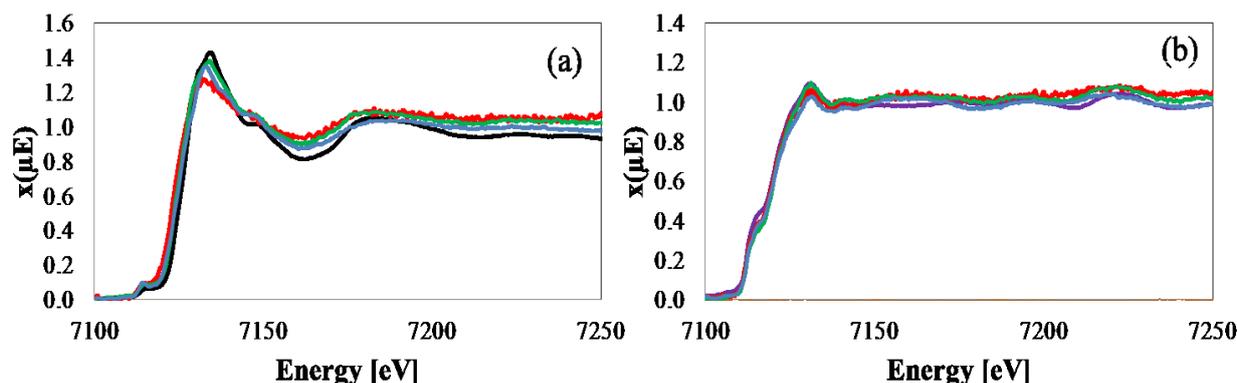


Figure 1: Fe K-edge XANES spectra of (—) Fe₂O₃-ZrO₂, (—) Fe₂O₃-CuO-ZrO₂ and (—) Ru doped Fe₂O₃-ZrO₂ acquired at 750 °C: (a) oxidized and (b) reduced. For comparison, XANES spectra of the reference materials (—) Fe₂O₃ and (—) Fe are also given.

The XANES data of the oxidized oxygen carriers (Figure 1a) show a pre-edge at ~7112 eV corresponding to the 1s → 3d electronic transition and a main absorption edge position at ~7120 eV corresponding to 1s → 4p electronic transition. These two edge values are in agreement with values reported in literature and characteristic for α-Fe₂O₃.⁵ Upon exposure to H₂, the oxygen carriers reduced to metallic iron (Figure 1b), as indicated by the increase in the intensity of the pre-edge feature at 7112 eV.

Figure 2 plots the change of the Fe K-edge XANES spectra during reduction for the three materials investigated. Each spectrum plotted in Figure 2 was acquired after a pulse of H₂ was released to the reactor. Initially, 50 pulses (duration 5 seconds) were sent to the reactor. This was followed by 50 pulses of 10 seconds duration and finally 25 pulses of 20 seconds duration.

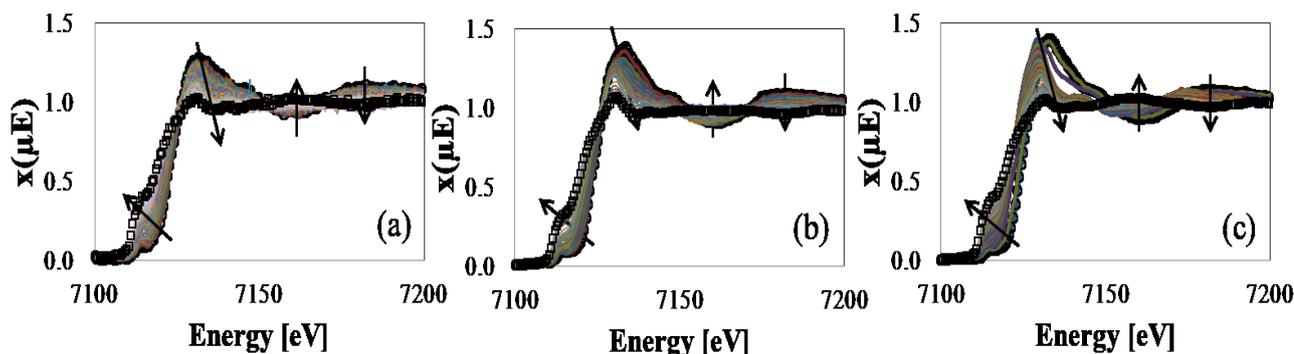


Figure 2: Time-resolved Fe K-edge XANES spectra for (a) Fe₂O₃-ZrO₂, (b) Ru doped Fe₂O₃-ZrO₂ and (c) Fe₂O₃-CuO-ZrO₂ for reduction at 750 °C. The circles (○) plot the initial, i.e. fully oxidized, state, whereas the squares (□) denote the final, i.e. fully reduced, state.

During reduction, the gradual change in the features of the XANES spectra in the absorption edge energy, as observed for all oxygen carriers, indicates the formation of intermediate iron oxides. During reduction, the

XAS spectra of the materials shift to lower energies since the binding energies of 1s electrons increase with an increasing valence state of Fe.⁶

The weight fraction of the different oxidation states of iron during reduction was determined using linear combination fitting. Figure 3 plots the reduction pathways of each of the materials.

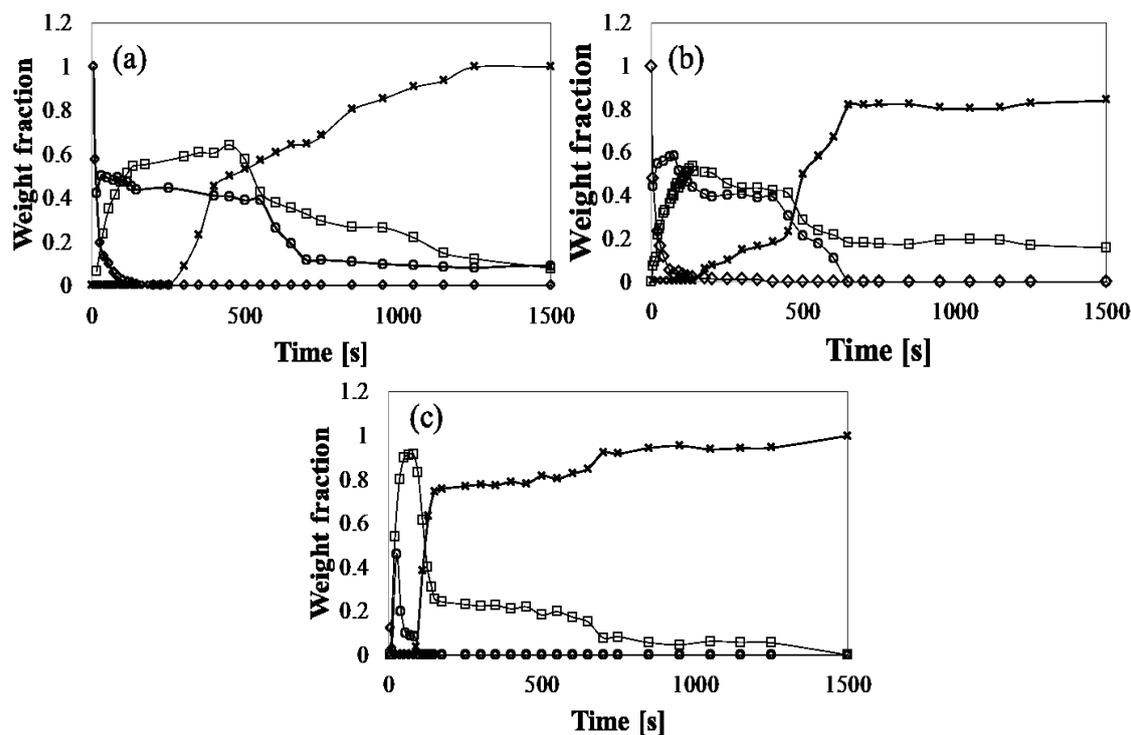


Figure 3: Phase evolution of the oxygen carriers with time during reduction for (a) Fe₂O₃-ZrO₂, (b) Ru doped Fe₂O₃-ZrO₂ and (c) Fe₂O₃-CuO-ZrO₂ for the reduction at 750 °C. The symbols denote the following iron phases: (◇) Fe₂O₃, (○) Fe₃O₄, (□) FeO, (×) Fe.

The first reduction step, *i.e.* Fe₂O₃ → Fe₃O₄, was very fast and not affected by the presence of Cu or Ru. On the other hand, promoting Fe₂O₃-based oxygen carriers with Cu increased the conversion rate of Fe₃O₄ to FeO and ultimately to metallic iron. Doping the oxygen carrier with Ru also accelerated the reduction steps although its influence was not as significant as for Cu.

4. Summary

In-situ Fe K-edge XAS was used to monitor the reduction pathways of Fe₂O₃-ZrO₂-based oxygen carriers. In particular, the effect of the addition of Cu and Ru on the reduction pathways and kinetics was critically assessed. The redox reactions were carried out at high-temperature (750 °C) using H₂ as the reducing gas. The XAS data were analyzed using linear combination fitting. The XAS spectra revealed that the formation of intermediate iron phases was significantly fast when Cu was added as a promoter. These results are important to model accurately the chemical looping process and to extract meaningful kinetic parameters.

5. References

1. Q. Imtiaz, A.M. Kierzkowska and C.R. Müller, ChemSusChem, 5 (2012) 1610.
2. Q. Imtiaz, A.M. Kierzkowska, M. Broda and C.R. Müller, Environ. Sci. & Technol. 46, (2012) 3561.
3. A.M. Kierzkowska, C.D. Bohn, S.A. Scott, J.P. Cleeton, J.S. Dennis, C.R. Müller, Ind. Eng. Chem. Res., 49, (2010) 5383.
4. S. Li, S. Krishnamoorthy, A. Li, G. D. Meitzner, E. Iglesia, J. Catal. (2002) 206, 202.
5. E. de Smit, A. M. Beale, S. Nikitenko, B. M. Weckhuysen, J. Catal., 262 (2009) 244.
6. S. Li, G. D. Meitzner, E. Iglesia, J. Phys. Chem. B., 105 (2001) 5743.