

	Experiment title: Structural and kinetic study of Mg-Fe-Al-O as novel oxygen carrier material for CO ₂ conversion	Experiment number: 26-01-1048
Beamline: BM26A	Date(s) of experiment : 25/09/2015 – 29/09/2015	Date of report: 18-11-2015
Shifts: 12	Local contact(s): Alessandro Longo	
Names and affiliations of applicants: Dr. POELMAN Hilde (+32 9 264 45 23, hilde.poelman@UGent.be) Dr. GALVITA Vladimir (vladimir.Galvita@UGent.be) Ir. DHARANIPRAGADA Aditya (aditya.dnvr@ugent.be) Ir. THEOFANIDIS Stavros, (StavrosAlexandros.Theofanidis@UGent.be) Prof. dr. ir. MARIN Guy B (Guy.Marin@UGent.be) Ghent University, Laboratory for Chemical Technology, Technologiepark 914, 9052 Ghent, Belgium		

Summary

A novel promoter material 10-Mg-Fe-Al-O showed remarkable stability and high CO yield towards a CO₂ utilization process[1]. The structural evolution during the reaction was investigated using in situ XRD, however no noticeable changes in the evolution of various iron oxide phases were observed. Hence, a detailed in situ XAS study was conducted on this material to identify the changes in oxidation state of iron oxides by probing around the Fe environment. The XAS study was performed along with in situ XRD study which could follow crystallographic changes in a six degree window. This could yield insight about the possible extraction of Fe through the lattice parameter evolution. The in situ XAS and XRD can provide information about the oxidation state evolution along with changes in local structure.

Experimental conditions

XAS measurements were performed at the Fe-K edge (7112 eV) in transmission mode. The redox properties of 10-Mg-Fe-Al-O were studied during H₂ reduction (up to 800°C), CO₂ reoxidation (up to 800°C). In situ XANES was performed to follow the oxidation state changes during these treatments. Further, EXAFS measurements were recorded before reaction, and at selected stages of treatments (after reduction and reoxidation). These steps will allow for modeling and hence supply quantitative structural information. In addition, EXAFS was measured at -196°C using a cryostat for selected samples.

Experiments performed and results

The oxidation state evolution was identified during XANES at Fe-K edge in 10-Mg-Fe-Al-O for fresh and 60 times cycled material during H₂-TPR and CO₂-TPO. The XANES of fresh material shows that during H₂-TPR a shift of edge and pre-edge occurred, indicating reduction, but the iron oxide was not completely reduced to metallic Fe (Figure 1a). The XANES evolution during the CO₂-TPO (Figure 1b) show that the material was oxidized back to its as prepared state (Figure 2).

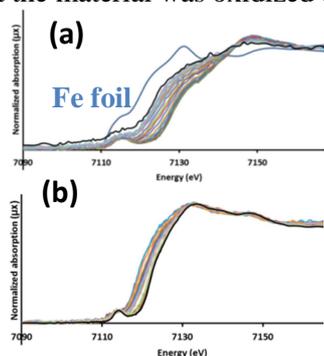


Figure 1: The Fe-K edge XANES spectrum up to 800°C of fresh 10-Mg-Fe-Al-O during (a) H₂-reduction and (b) CO₂-reoxidation

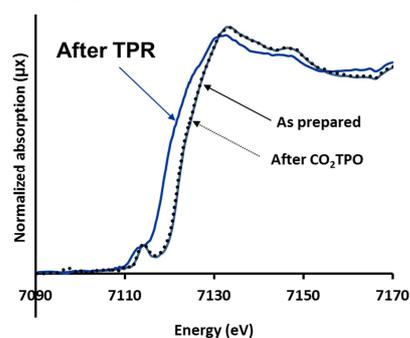


Figure 2: The room temperature XANES spectra of 10-Mg-Fe-Al-O in as prepared state, after H₂-TPR and after CO₂-TPO.

The diffraction changes were followed during reduction and reoxidation in a six degree window around the main spinel diffraction position. They show a slight decrease in lattice parameter during H₂-TPR (Figure 3a). In addition to thermal expansion, which gives rise to a downward shift of diffractions, the observed shift in TPR could point to reduction and/or Fe extraction from the spinel lattice. A more complex variation occurs during CO₂-TPO.

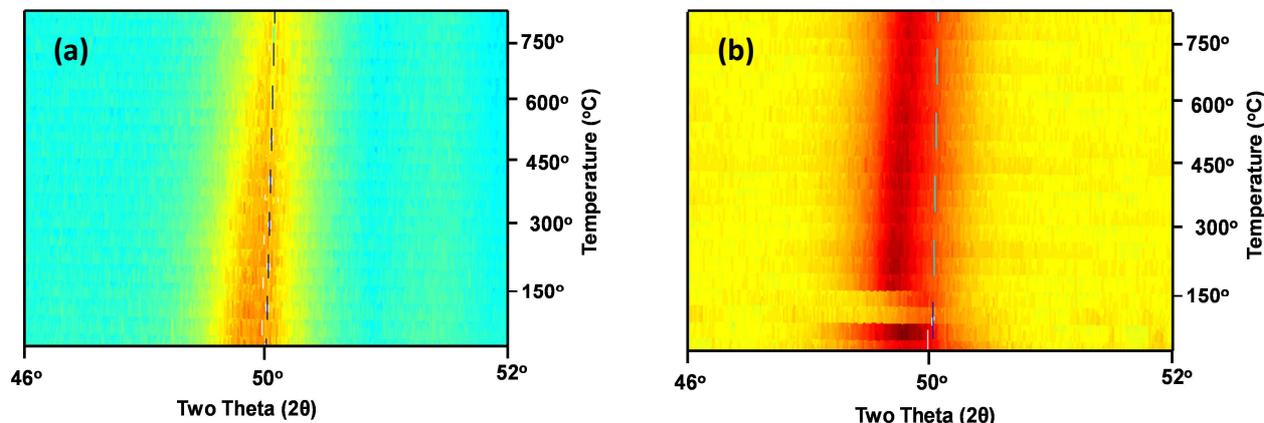


Figure 3: High resolution in situ XRD pattern of the most intense diffraction peak of 10-Mg-Fe-Al-O at Fe-K edge during (a) H₂-reduction and (b) CO₂-reoxidation

Further, for the 60 times cycled sample, a room temperature XANES spectrum after H₂-TPR and CO₂-TPO shows that the material did not oxidize back to the as prepared state (Figure 4). This could be due to the prolonged cycling which could result in deactivation. Comparison with references of Fe₂O₃ and Fe₃O₄ show that these materials are electronically different. The pre-edge features show that in both fresh and cycled material Fe is distributed in octahedral and tetrahedral sites, as they exhibit sharper pre-edge peaks. EXAFS of fresh and 60 times cycled sample at -196°C, yield k-space features (Figure 5) with clear structural differences from the reference materials (Fe₂O₃ and Fe₃O₄). Further analysis of the pre-edge features and the k-space signals will allow for detailed modelling of the second shell, which will yield structural insight in the material.

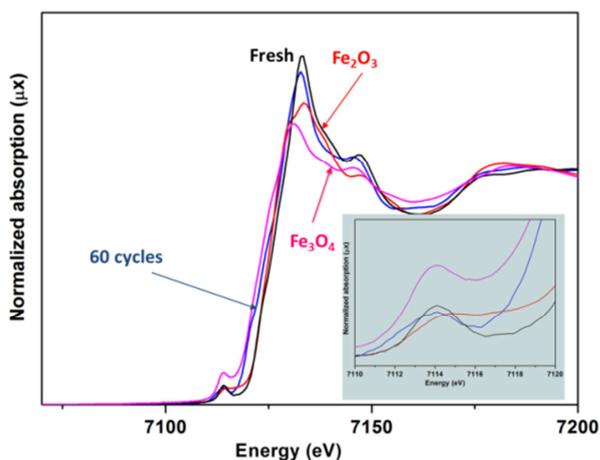


Figure 4: XANES of the fresh and cycled sample, the latter after TPR and TPO, with references Fe₂O₃ and Fe₃O₄, and the inset showing pre-edge features of all these materials.

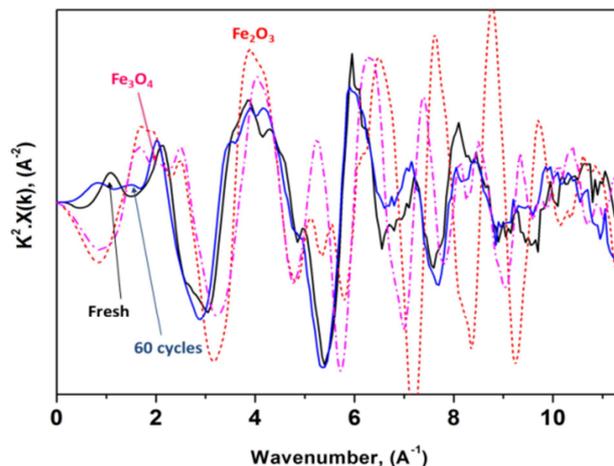


Figure 5: The k-space spectra of the fresh and cycled material, the latter after TPR and TPO, with references Fe₂O₃ and Fe₃O₄ measured at -196°C.

References

- [1] A.N.V.R. Dharanipragada, L. Buelens, H. Poelman, E. De Grave, V. Galvita, G.B. Marin, J Mater Chem A (2015).