ESRF	**Experiment title:** **IRON OXIDE BASED MATERIALS AS OXYGEN CARRIERS FOR AN ENVIRONMENTALLY SUSTAINABLE PRODUCTION OF H2 FROM FOSSIL FUELS**	**Experiment number**: CH-1333
Beamline: BM08	**Date of experiment**: from: 03/10/2002 to: 07/10/2002	**Date of report**:
Shifts: 12	**Local contact(s)**: Carlo Meneghini	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Gilberto Artioli*, Mauro Gemmi*, Marco Merlini* Università di Milano

Claudio Contardi*,Ugo Cornaro*, Danila Ghisletti* Enitecnologie, S.Donato Milanese

Report:

The development of an "hydrogen economy" foreseen for the middle of the century is a possible answer to the needs of a sustainable economic growth. In the medium term hydrogen production will still rely on fossil fuels whose environmental impact has to be smoothed both modifying actual technology and/or developing new ones capable to mitigate CO_2 emission. ENI[1] is developing an innovative technology (One Step Hydrogen) for H_2 production from fossil fuels with an inherent confinement of CO_2 in a concentrated stream, ready to be buried.

The process is based on the properties of selected oxides that once reduced with hydrocarbons, are capable to be re-oxidized by splitting H_2O into H_2 and [O], which in turn re-oxidizes the solid closing the loop. Iron oxide has been proposed as a viable oxygen carrier. Suitable choice of a support and a deep understanding of reduction mechanism are key issues for a successful technology development.

In situ X-ray powder diffraction studies, combined with the simultaneous analysis of the evolved gas products (i.e. H_2, CO_2, etc.) are fundamental to understand the behaviour of the crystalline phases involved in the process, in particular the phase changes in the catalyst phases, the partial reaction of the carrier phases, and ultimately the reaction mechanisms.

The system investigated is an iron oxide based material loaded on CeO_2-ZrO_2 based support. During the reaction, the hematite is reduced to magnetite, wustite, iron and finally cohenite (Fe_3C).

The simultaneous in situ experiment was performed in isothermal mode at different temperature at the CRG beam line BM8 at ESRF, Grenoble. A translating image plate set up was used for the diffraction characterization of the solid state phases[2] , whereas the evolved gas products were analyzed using a mass spectrometer connected with the capillary reaction chamber. The catalyst in the capillary was maintained under an appropriate gas flow (air, Ar, mixture of CH_4 and Ar) using a remotely controlled system appropriately prepared. The sample was heated by a hot gas blower. Monochromatic radiation of 25 keV was selected to have an optimal compromise between beam transmittance and d-space resolution. The time resolution of each isothermal run was gauged by proper choice of the IP translation speed.

Rietveld analysis of the collected powder spectra allowed complete identification and quantification of the phases formed during the combustion reaction and during cooling. The simultaneous mass spectrometry measurements allowed synchronization of the information obtained in the solid phases and those obtained on the gas phases. Evolution of hydrogen is linked to the transformation of magnetite into reduced-Fe phases (Fig. 1). The reaction rate at different temperatures is controlled by the exchange of oxygen between the Fe catalysts and the supporting non-stoichiometric CeO_2 phase.

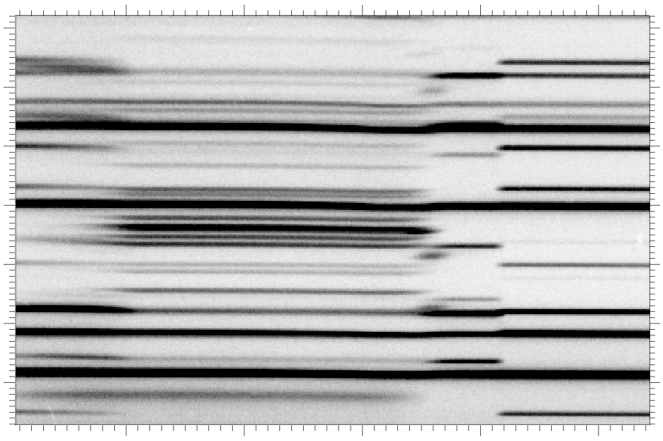

Fig. 1a – Isothermal run recorded by image plate

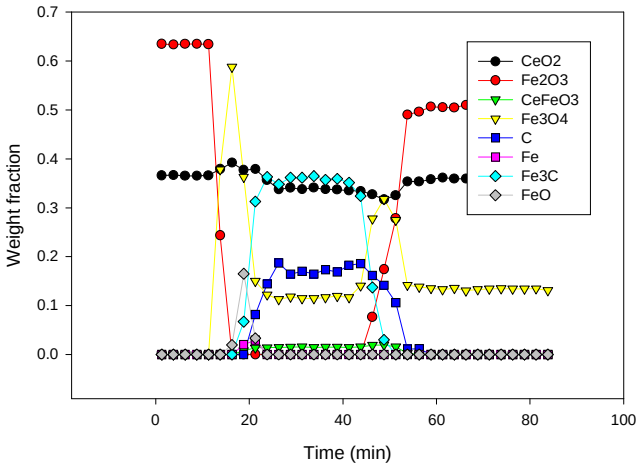

Fig. 1b –Weight fractions of the crystalline phases vs. time, calculated by Rietveld methods

REFERENCES

[1] *EP 1134187 (19/09/2001) to Snamprogetti*

[2] *Meneghini C., Artioli G., Balerna A., Gualtieri A.F., Norby P., Mobilio S.: Multipurpose imaging plate camera for in-situ powder XRD at the GILDA beamline. Journ. Synchrotron. Rad. 8, 1162-1166, 2001*