



	<b>Experiment title:</b> IN SITU EXAFS STUDY OF PROMOTED CeO <sub>2</sub> -ZrO <sub>2</sub> MIXED OXIDE CATALYSTS FOR PARTIAL OXIDATION OF ALKANES	<b>Experiment number:</b> CH-980
<b>Beamline:</b> BM29	<b>Date of experiment:</b> from: 13-09-2000 to: 18-09-2000	<b>Date of report:</b> 29-08-2001
<b>Shifts:</b> 15	<b>Local contact(s):</b> STUART ANSELL	<i>Received at ESRF:</i>
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## Report:

We made use of the 15 shifts assigned to this new project to study, by EXAFS spectroscopy, two series of CeO<sub>2</sub> based catalysts in the investigation of catalytic materials and processes for the direct transformation of light hydrocarbons contained in natural gas into oxygenates (alcohols, epoxides, aldehydes ...). The study is aimed at producing the oxygenates without the intermediate formation of olefins or synthesis gas. The design of systems able to perform this task requires non conventional materials in order to get high selectivity toward partially oxygenated products avoiding the prosecution of the oxidation reaction to the complete combustion products (H<sub>2</sub>O e CO<sub>2</sub>).

X-ray absorption spectra were collected at the BM29 beamline, equipped with a Si(311) double crystal monochromator. All spectra were recorded at 300 K in transmission mode at the Ce K-edge over the range 40.0-41.8 keV, with a sampling step of 1 eV and an integration time of 2 s for each point. Incident and transmitted photon fluxes have been detected with ionisation chambers filled with Kr. Each spectrum has been acquired three times. The samples were loaded in standard Al sample-holders (6 mm thickness) and measured as-such. Sample homogeneity was checked by reading the transmitted photo-current while scanning the sample area along the x-y axes. Extracted  $\chi(k)$  data have been averaged before the EXAFS data analysis and error bars have been evaluated from the experimental standard deviations. Experimental  $\chi(k)$  data were extracted from absorption data by a conventional procedure. The  $k^3$ -weighted  $\chi(k)$  data were Fourier transformed over a Kaiser window, with  $\tau=2.5$ , in the  $k$  range of 3-15 Å<sup>-1</sup>. Main contributions to the Fourier transform modulus were filtered in order to obtain metal nearest-neighbour shells. The so obtained filtered contributions were analysed using the programs developed by Michalowicz. Phase shift and amplitude

functions of scattering atoms have been extracted from the experimental spectra of the model compound  $\text{CeO}_2$  (fluorite structure: 8 O at 2.34 Å and 12 Ce at 3.83 Å). The two systems measured during the 2000 beamtime allocation are:

-  $\text{Ce}_x\text{-Zr}_{1-x}\text{O}_2$  systems prepared with different: Ce/Zr ratios and oxide preparation route (coprecipitation, mechanical grinding). Oxygen absorption/desorption measurements have evidenced that the oxide composition is strongly dependent on the oxygen partial pressure: in anaerobic condition in presence of the alkylic substrate the stoichiometric ratio decreases down to 1.7, as these oxidic systems are able to selectively transfer to the hydrocarbons feed flow the atomic oxygen stored in their crystal structure during a previous reaction step. The redox behaviour has been studied in reaction cycles oxygen-hydrocarbon with methane, ethane and propane, and the process is quantitatively reversible after several cycles. EXAFS spectra have been recorded before and after each reaction step, using different hydrocarbon feed, in order to follow the oxygen coordination variation around the Ce and Zr atoms under oxygen or hydrocarbon atmosphere, and so the degree of ion mobility and crystal defectivity.

-  $\text{CeO}_2$  and  $\text{Ce}_x\text{-Zr}_{1-x}\text{O}_2$  systems supported on high surface area  $\gamma\text{-Al}_2\text{O}_3$  with the aim of studying the alumina stability operated by ceria under reducing or reducing/oxidizing conditions and of elucidating the actual mode of operation of ceria; in fact, although it is very well known that its main feature relies on the redox couple  $\text{Ce}^{4+}/\text{Ce}^{3+}$ , a complete knowledge of the structural and morphological evolution of  $\text{CeO}_2$  deposited on alumina has yet to be acquired. Our preliminary results indicate that there is a remarkable stabilization effect operated by ceria when treated under hydrogen containing atmospheres at high temperatures, evidencing an important role of  $\text{Ce}^{3+}$ . From the BET surface areas of  $\text{Al}_2\text{O}_3$  and ceria-supported  $\text{Al}_2\text{O}_3$  after treatment under air for 6 h in the temperature range from 1273K to 1473K, it can be seen that, the stabilization effect of ceria under oxidizing conditions is effective only in a narrow temperature range around 1373K, and is strongly dependent on loadings, with the lowest loadings (2-5%) performing better than the highest (12-25%). A comparison of  $\text{CeO}_2$  with  $\text{La}_2\text{O}_3$  shows that  $\text{La}_2\text{O}_3$  has a superior stabilizing effect, especially at high temperatures where  $\text{CeO}_2$  is almost entirely ineffective. The reason for stabilization operated by  $\text{La}_2\text{O}_3$  on  $\text{Al}_2\text{O}_3$  is that it prevents the formation of  $\gamma\text{-Al}_2\text{O}_3$ . The mechanism by which this occurs is most likely to be related to the formation of microdomains of lanthanum aluminate on the alumina surface, which will lock highly reactive coordinative unsaturated Al ions into a thermally stable structure. The above model can readily be extended to cerium, since  $\text{LaAlO}_3$  and  $\text{CeAlO}_3$  are isostructural oxides with similar lattice parameters. This can be done by increasing the amount of cerium present in the reduced form as  $\text{Ce}^{3+}$ .  $\text{CeO}_2/\text{Al}_2\text{O}_3$  samples previously calcined at 1073K for 6 h were therefore subjected to reduction treatment under 5%  $\text{H}_2/\text{Ar}$  atmosphere at 1473K for 6 h. After this treatment, the surface area of alumina stabilized to values of ca. 60-70  $\text{m}^2/\text{g}$ . Correspondingly, TPR measurements indicate a significant formation of  $\text{Ce}^{3+}$ . The comparison with the reduction profile of pure ceria shows a peak at higher temperature which is tentatively due to formation of bulk  $\text{CeAlO}_3$ . EXAFS data of reduced samples identify the presence of  $\text{CeAlO}_3$  with no traces of  $\text{CeO}_2$  phases, which represent the majority in samples treated under oxidizing conditions. The remarkable stability effects operated by ceria under these conditions (elevated surface area and prevention of  $\alpha\text{-Al}_2\text{O}_3$  formation, as measured by XRD diffraction) are identical to those operated by  $\text{La}_2\text{O}_3$  under oxidizing conditions, especially at the highest temperatures. In addition, a partial stabilization is preserved after thermal reductive-oxidative treatment at high temperature. This is a consequence of the presence of residual  $\text{Ce}^{3+}$ , which is not totally oxidized to  $\text{Ce}^{4+}$  even after processing under oxidizing conditions. In agreement with TPR measurements, EXAFS data indicate that after a redox cycle (i.e. oxidation at 1073K for 6 h, reduction at 1473K for 6 h and oxidation at 1473K for 6 h) approx. 5% of cerium is still present as  $\text{Ce}^{3+}$  on samples with 15%  $\text{CeO}_2$ . The presence of  $\text{Ce}^{3+}$  also explains partial stabilization under oxidizing conditions on low loaded samples, which is related to the formation of some dispersed  $\text{CeAlO}_3$  on the surface of  $\text{Al}_2\text{O}_3$ . After ageing under air at 1273K, 1373K and 1473K, the oxygen coordination numbers suggest that approx. 25, 10, and 1% of cerium on 15%  $\text{CeO}_2/\text{Al}_2\text{O}_3$  is present as  $\text{Ce}^{3+}$ . As this amount increases as  $\text{CeO}_2$  loading decrease, the partial stabilization of  $\text{Al}_2\text{O}_3$  operated by ceria under oxidizing conditions seems therefore to be effective only if  $\text{Ce}^{3+}$  is formed on the surface.

The previous results produced a work that will shortly be submitted to the Journal of Catalysis. We sincerely thank the BM29 beamline staff for their kind and competent assistance.