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Experiment Report Form

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.

(next page)



	Experiment title: Combining XAS with on-line GC catalytic studies for in situ characterization of Volatile Organic Compounds (VOCs) elimination over a CuO-CeO ₂ /Al ₂ O ₃ catalyst	Experiment number: 26-01-760
Beamline: BM26A	Date(s) of experiment: From: 07-12-2006 To: 12-12-2006	Date of report: 31-8 -2007
Shifts: 15	Local contact(s): Dr. Serge NIKITENKO	
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Report:

The aim of the experiment was to study the changes in the structure and catalytic activity of the CuO-CeO₂/Al₂O₃ catalyst during the total oxidation of propane by an *in situ* method, which combined X-ray absorption spectroscopy (XAS) and gas chromatography (μ -GC). The XAS study was performed in transmission mode at the Cu K edge (i.e. 8979 eV) and was coupled with kinetic measurements, which were carried out under different working conditions (i.e. temperatures and space times). A new type of X-ray absorption cell that serves also as a catalytic reactor^[i] was used to perform the experiments.

Depending on the reaction feed, these experiments can be divided into two categories:

- with the catalyst under simultaneous flow of propane in He (5% C₃H₈/He) and oxygen (keeping the propane to oxygen ratio constant at 5, which is the stoichiometric ratio for this oxidation reaction)
- with the catalyst under flow of 5% C₃H₈/He (reductive conditions)

Before starting the reaction experiments, the grounded catalyst (< 20 μ m) was diluted with boron nitride (dilution degree (wt.): 0.69 g BN/g {cat. + BN}) in order to have a detectable amount of transmission out of the sample and this mixture was loaded in the form of compacted powder into the experimental cell and was pre-treated as follows. First, the sample was heated under He flow from room temperature to 413 K. Next, at this temperature the sample was kept under air flow for approximately one hour. At last, the catalytic system was further heated in He flow until it reached the first reaction temperature. As it was expected from our previous studies^[ii], this pretreatment did not alter the local Cu structure of the catalyst.

By adjusting the inlet molar flow, three different space times (namely 61.5, 76.4 and 94.5 kg_{cat} s mol⁻¹) could be obtained for each reaction temperature. The reaction temperature range that was used varied from 593 K to 753 K and the experimental cell was operating under atmospheric pressure. Propene, CO and CO₂ were found to be the main reaction products. Propane conversion and selectivities to different products were calculated assuming 100% carbon balance. X-ray absorption spectra of the catalytic system were recorded during the whole experimental procedure. Moreover, the Cu references, Cu foil, CuO and Cu₂O, were measured at room temperature, with the later two being measured in the same cell as the one used for the experiments. From the spectra of these references a linear correlation between the Cu valance and the white line position was found (see Figure 1), which served as a tool for the XANES analysis.

Although it was initially proposed to take EXAFS spectra of the catalytic system under working conditions, during the XAS measurements it was observed that the signal to noise ratio was rather poor. So it was decided to limit the XAS measurements to the XANES region, where the quality of the spectra could be improved by averaging. The same averaging procedure could not be applied for the EXAFS spectra, as the oscillations of the EXAFS region were masked by the noise of the measurement, leading to the fact that no information could be obtained from them. XANES spectra were mainly recorded in the quick scanning mode (i.e. 1 min scans), in order to have the best possible time resolution when new conditions are applied to the catalytic system. For improving the quality of the spectra about 40 noisy spectra had to be averaged, which corresponds to a 40 min time period. Therefore, catalytic changes occurring on very small time scales, such as the reduction of the catalyst, could not be accurately monitored due to the necessary averaging of the spectra. Averaging can be applied in cases where the reaction takes place under steady state conditions, which is true for the first type of experiments. Bearing in mind these considerations, the analysis of the obtained data was performed and the following findings can be reported.

For the first type of experiments, a first visual comparison (see Figure 2) between the spectra of the catalyst obtained at different temperatures and space times and the spectrum of the oxidized sample showed almost no differences. Additionally, in most cases the average of 40 spectra yielded a valence estimate of 2. However, due to the poor signal-to-noise ratio of the spectra the uncertainty on this estimate is rather large and an error of about 0.5 has to be considered. In Figure 3a, the evolution of the selectivity and propane conversion with time on stream is given only for the first reaction temperature studied and at the three space times. As the catalytic system experiences for the first time a combined flow of propane and oxygen, the selectivity to CO₂ increases to the expense of the selectivity to CO, until they both reach thermodynamic equilibrium. On the other hand, the selectivity to propene reaches a constant value almost from the beginning. Both observations agree with a parallel-consecutive scheme of hydrocarbon oxidation (see Figure 3b), in which propene reacts fast enough on the metal oxide surface to form total oxidation products while the CO → CO₂ reaction occurs slower. In accordance with this reaction scheme, a decrease in space time leads to a decrease in propane conversion and in selectivity to CO₂, while the selectivities to CO and to propene are slightly increased.

For the second type of experiments, Figure 4 presents the dynamic structural changes during the reduction of the catalyst with propane. A full reduction of the Cu²⁺ towards metallic Cu⁰ occurs and careful examination of the edge of the XANES spectra reveals that a small amount of Cu¹⁺ appears (see r33076 in figure).

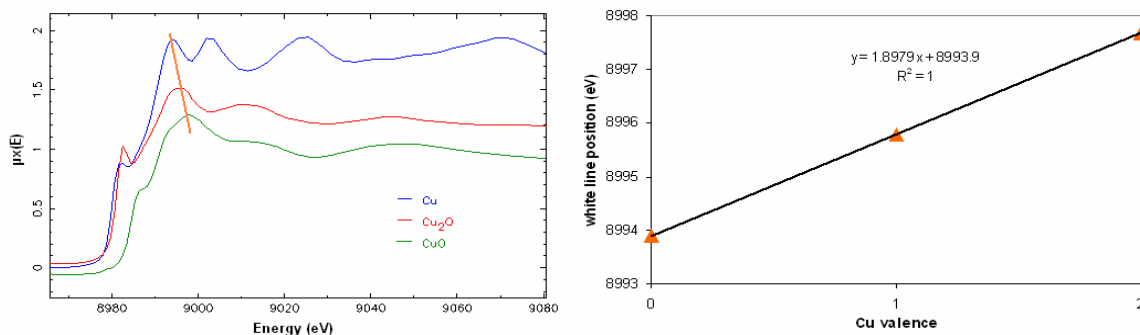


Figure 1. XANES spectra for the CuO, Cu₂O and Cu references together with the linear relationship that has been determined between the white line position and the Cu valence

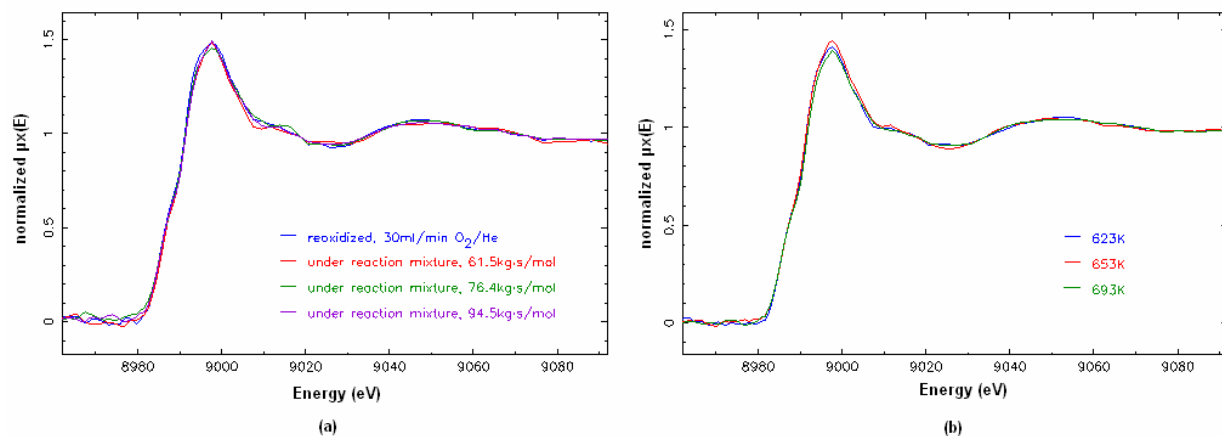


Figure 2. Averaged XANES spectra of the catalyst during steady state reaction conditions, (a) at different space times with the temperature constant at 693 K, (b) at different temperatures and fixed space time at 94.5 kg/s/mol

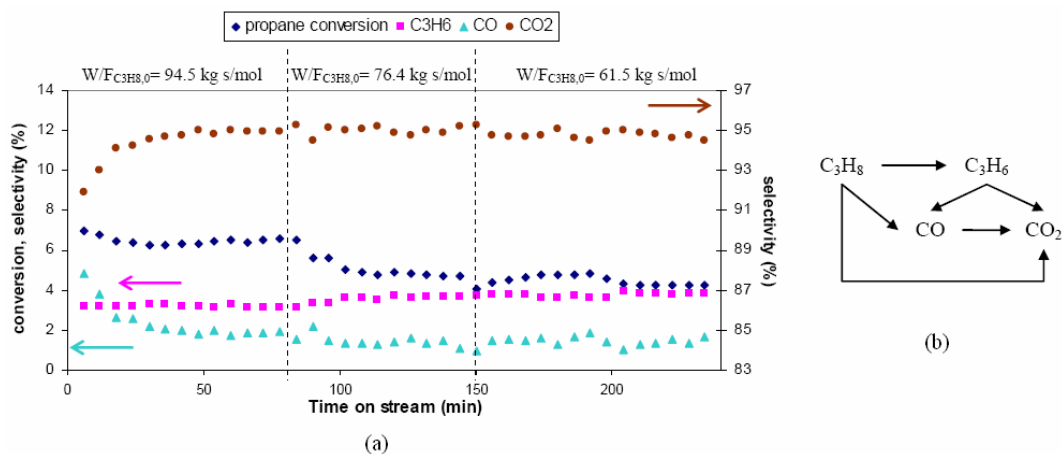


Figure 3. Selectivity to different products and propane conversion at atmospheric pressure and at 623K while feeding simultaneously propane and O_2 (with a molar ratio of $O_2:C_3H_8 = 5:1$) and decreasing space time (at $t=0$ the catalytic system is for the first time under this reactant flow), (b) Parallel-consecutive reaction scheme

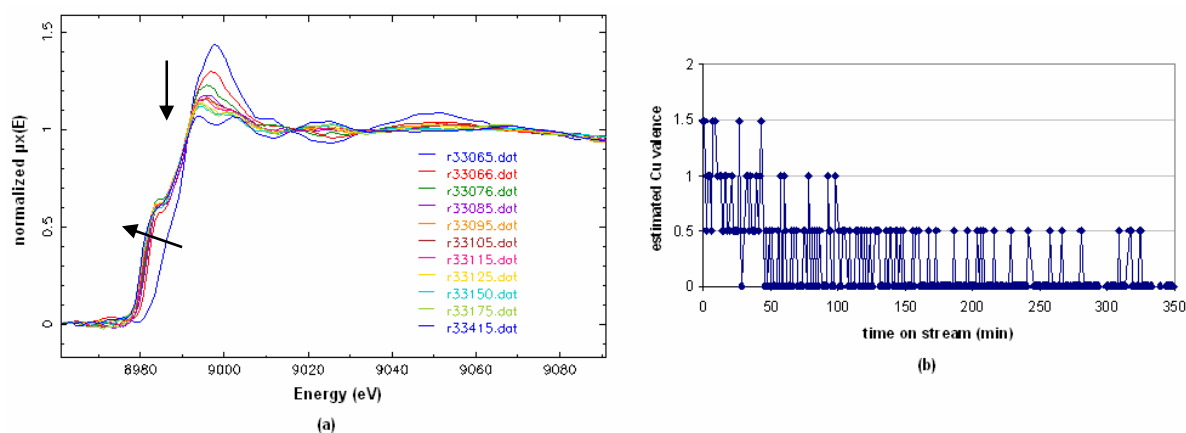


Figure 4. (a) XANES spectra of the catalyst during a long treatment with propane and with increasing the temperature stepwise from 693 K to 753 K, (b) evolution of the estimated Cu valence (from the 1min scans) during the treatment with propane (the variation of this estimate due to the noise in the spectra is observed)

ⁱ J.-S. Girardon, A.Y. Khodakov, M. Capron, S. Cristol, C. Dujardin, F. Dhainaut, S. Nikitenko, F. Meneau, W. Bras, E. Payena, J. Synchrotron Rad. 12 (2005) 680.

ⁱⁱ G. Silversmit, H. Poelman, M. Olea, V. Balcaen, P.M. Heynderickx, S. Nikitenko, W. Bras, D. Poelman, R. De Gryse, G. B. Marin, in preparation.