DUBBLE

ESRF

Experiment title: Total oxidation of propane over CuO-CeO2/Al2O3 catalyst : Structure-activity relationship of metal oxides using XAFS coupled with mass spectrometry

Experiment number: 26-01-860

Beamline: BM26A

Date(s) of experiment : 4-9/11/2009

Date of report: 4/11/2010

Shifts: 15

Local contact(s): Sergey Nikitenko

Names and affiliations of main applicants:

Dept. Chemical Engineering, Laboratory for Chemical Technology, Krijgslaan 281, S5, 9000 Ghent Belgium, Fax +32 (0)9 264 4999
Prof. dr. ir. **MARIN Guy b.** Phone +32 9 264 4517, Email : Guy.Marin@UGent.be
dr. **POELMAN Hilde** Phone +32 9 264 43 71 Fax +32 9 264 49 96, Email: hilde.poelman@UGent.be

Dept. Solid State Sciences, LumiLab, Krijgslaan 281, S1, 9000 Ghent Belgium, Fax +32 (0)9 264 4996
Prof. dr. **POELMAN Dirk** Phone +32 9 264 43 67, Email: dirk.poelman@ugent.be

Report: (max. 2 pages)

Introduction

The aim of the experiment was to investigate the structure-activity relationship of a CuO-CeO_2/Al_2O_3 catalyst in propane total oxidation and redox treatments by an *in-situ* method, combining absorption spectroscopy (XAS) at Cu K and Ce L_{III} and on-line catalytic measurements using mass spectrometry (MS).

Experiments performed

With undiluted catalyst loaded into a reactor capillary of 0.8 mm outer diameter, good quality XAS spectra were obtained: for Ce LIII edge, XANES was measured up to k = ~ 4 $Å^{-1}$, while for Cu K edge EXAFS was recorded to k = ~ 8 $Å^{-1}$. Gas-phase compositions were obtained, using a calibrated MS (Omnistar^{TM}).

For both Cu and Ce, isothermal experiments were performed consisting of catalytic red/ox cycles with C_3H_8/He or H_2/He and O_2/He resp.. Further, total oxidation reactions were carried out under simultaneous flow of propane and oxygen with ratio 1:10 for 3 space times at 3 temperatures.

Results

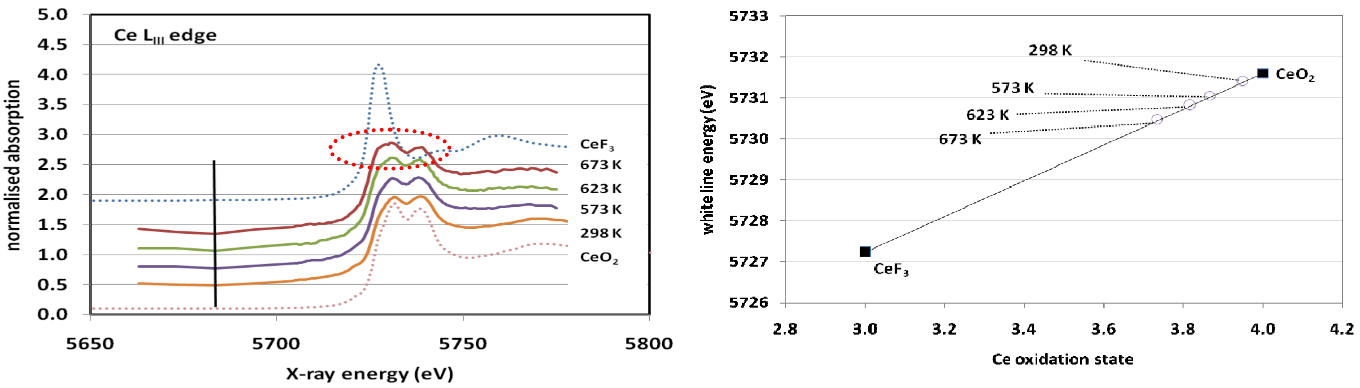

Fig. 1: left: *Ce L_{III} XANES for isothermal reduction cycles ((solid lines, 5% C_3H_8/He, 1.86 10^{-7} mol C_3H_8/s); reference spectra in dotted line); straight line: position of glitch in pre-edge region used for alignment;* ***right:*** *WL of the Ce L_{III} edge XANES spectra. solid squares: energy position of the WL for CeF_3 and CeO_2 (3+ and 4+, resp.); solid line: linear relationship between WL energy position of references and their oxidation state; open circles: energy position of the Ce L_{III} WL of CuO-CeO_2/Al_2O_3 during propane reduction.*

Isothermal reduction with 5% C_3H_8/He in 50K steps up to 673K (400°C) caused the Cu to reduce completely to Cu^0, passing through an intermediate oxidation state of 0.9±0.2 at T = 623K (not shown). The Ce edge started showing effect of the propane reduction at the highest temperature 673 K (Fig 1a). White line analysis (WL) of this edge yielded a steadily decreasing value of average oxidation state, to reach 3.73 ± 0.07 at a temperature of 673 K. This means that about 27 % of the Ce is then present as Ce^{3+}.

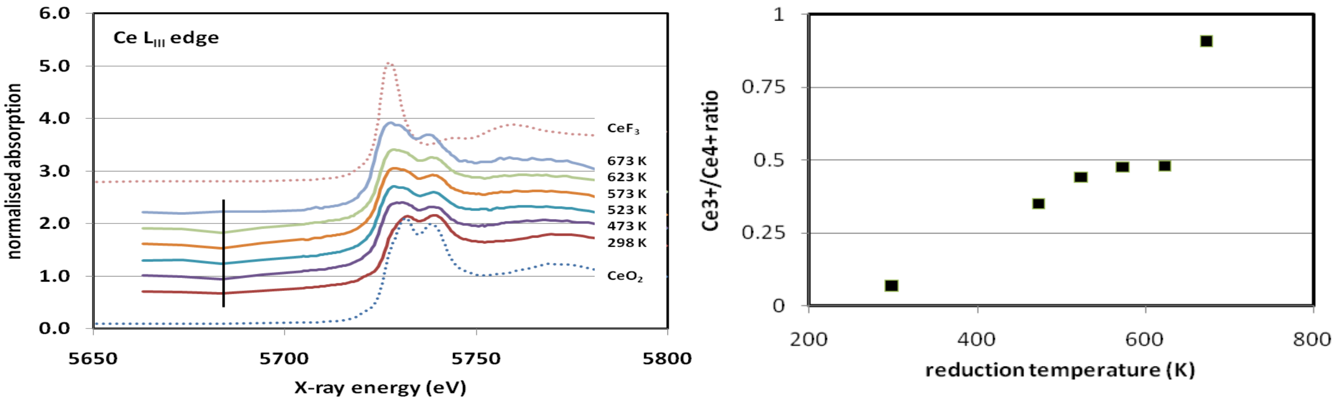

***Figure 2: left:** isothermal hydrogen reduction of the catalyst $CuO-CeO_2/Al_2O_3$ followed at the Ce L_{III} edge; line = glitch used for alignment (solid lines, 5% H_2/He, 1.86 10^{-7} mol H_2/s); reference spectra in dotted line; **right:** ratio Ce^{3+}/Ce^{4+} of contributions in the XANES spectra during isothermal H_2 reduction versus reduction temperature as result of a LCF XANES spectra with Ce^{4+} and Ce^{3+} references as standards*

Isothermal reduction with 5% H_2/He abruptly changed the copper phase in the catalyst from CuO to Cu between 473 K and 523 K. The Ce L_{III} XANES started changing from 473 K on and progressed further than with propane. A linear combination fit (LCF) was performed on the XANES spectra using the Ce^{4+} and Ce^{3+} reference spectra as standards and resulted in a variation of Ce^{3+}/Ce^{4+} ratio versus reduction temperature as in figure 2b. At the first temperature 473 K, 26 ± 1% of the observed Ce is already in 3+ oxidation state. This is observed mainly in the first white line, which shifts to the left (lower energy) and tends to develop a shoulder. The amount of reduced Ce further grows with increasing temperature to reach 0.48 ± 0.04, i.e. almost half of the Ce species is reduced at 673 K.

During total oxidation experiments no changes occur in XANES, indicating that both Cu and Ce remain fully oxidized during reaction (not shown). From the MS measurements, the conversion of propane could be obtained as function of space time, leading to an Arrhenius plot which yielded an apparent activation energy of 68.74 KJ/mol (Fig. 3 left). Simulating the data with the Mars-van Krevelen mechanism in a plug flow reactor yielded a reasonable correlation between experimental and calculated data (Fig. 3 right).

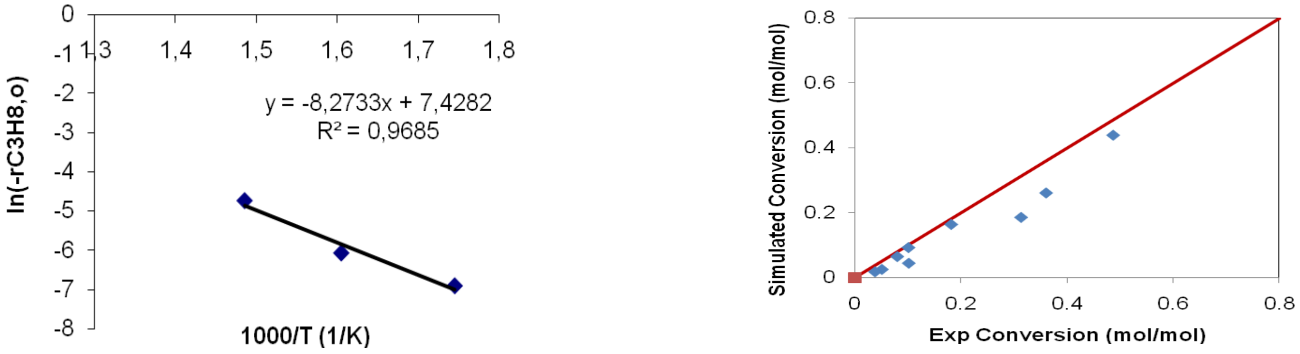

***Fig. 3: left:** Arrhenius relation for the total oxidation of $CuO-CeO_2/Al_2O_3$ with $C_3H_8:O_2$ feed in 1:10 ratio; **right :** Parity plot based on Mars-van Krevelen mechanism for catalyst total oxidation reaction results.*

Conclusions

From the above it is clear that in catalytic reactions with a $CuO-CeO_2/Al_2O_3$ catalyst, the CeO_2 promoter is not a spectator but takes actively part in the reaction. Reduction experiments with propane or hydrogen show a clear partial reduction of the CeO_2 at temperatures close to those where CuO is being reduced. Whether CeO_2 directly reacts with the gas phase or supplies oxygen to the reduced CuO phase, needs to be determined. The total oxidation behaviour of the catalyst can be described reasonably with the Mars-van Krevelen mechanism. The results described here are currently being processed for publication.