EUROPEAN SYNCHROTRON RADIATION FACILITY
ESRF User Office
BP 220, F-38043 GRENOBLE CEDEX, France
Delivery address: 6 rue Jules Horowitz, 38043 GRENOBLE, France
Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr

Nature and in-situ evolution of Cu species supported on SiO_2-MgO catalysts for the conversion of ethanol into 1,3-butadiene

Proposal Summary (should state the aims and scientific basis of the proposal):
SiO_2-MgO materials are promising catalysts for the production of green 1,3-butadiene, a key commodity chemical, via the one-step gas-phase conversion of ethanol (i.e. the Lebedev process). We have previously found that the use of CuO as promotor led to a much improved conversion and selectivity to butadiene, which was tentatively attributed to a boost in acetaldehyde formation, a key intermediate in the reaction mechanism, as a result of improved dehydrogenating activity of the catalysts. To understand this substantial increase in activity and to further improve the catalyst, we attempt to elucidate the nature of the copper species formed. Traditional characterization techniques, e.g. TEM and UV-Vis studies, did not allow us to determine the size and chemical identity of the deposited copper species. The low amount of Cu employed (calculated as 1 wt% of CuO) furthermore precludes their study with techniques, such as X ray diffraction (XRD). Finally, any possible changes in the copper species under reaction conditions need to be determined, as these can be related to the observed catalyst deactivation. Therefore, the main objective of this study is twofold: i) elucidation of the nature of Cu species (oxidation state and coordination number) supported on SiO_2-MgO used for the ethanol-to-butadiene Lebedev process and ii) the study of the oxidation state of Cu species during reaction.

Scientific background:
Fossil feedstock depletion together with a continuous increase in energy demand and chemical building blocks drives the attention of scientists to investigate renewable resources. Bio-ethanol (produced via fermentation of sugars) is considered one of the most promising feedstocks to respond to this increased demand. The one-step Lebedev process could provide the means to synthesize the important polymer building block butadiene from bioethanol in a green and sustainable way.[i]
CuO/SiO_2-MgO catalysts have shown high activity and selectivity in this reaction. In order to better understand the role of copper, different electron microscopy techniques were employed such as bright field and dark field TEM (transmission electron microscopy), HAADF (high angle annular dark field)-TEM, but no Cu particles could be identified. This could be due to the small particle size of any deposited Cu species, the formation of a solid solution, or most probably to an inherent lack of contrast of the material used. The use of TEM combined with EDX (energy dispersive X-ray analysis) did show that copper oxide is present on both silica- and magnesia-rich areas, though, thus showing no preferential location of copper on either of the two components of the catalysts (Figure 1).

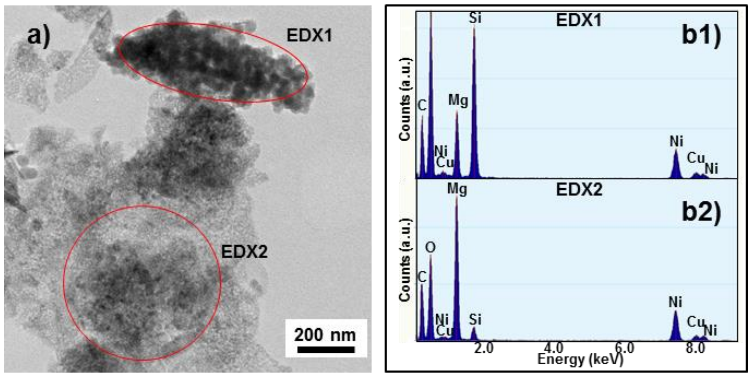

Figure 1. a) TEM picture of a Cu-promoted SiO_2-MgO catalyst used for the Lebedev process. No copper particles can be seen, but EDX analysis (b1, b2) shows copper to be present in both the SiO_2-rich and MgO-rich regions.

UV-Vis spectroscopy can prove really useful to study changes in electronic state of (transition) metal ions. In our case, various features were observed for different CuO-containing catalysts (Figure 2); the most interesting features were thought to arise from: 1) isolated CuO species supported on the two different components (region a, Figure 2); 2) cluster-like Cu-O-Cu species of varying size (region b, Figure 2).

Importantly, absorption in the latter region was observed to be more intense for those catalysts, which proved more active in the Lebedev process (Figure 2b).
Even though the UV-Vis spectra do provide insight into the nature of the Cu species on the catalyst, it could not be clarified if the Cu species are particles or clusters that are too small to be observed with TEM or if a solid solution with the MgO phase is formed. To establish a structure-activity relationship, the nature of the CuO species needs to be determined, however; promisingly, a previous study on a different system showed that a similar problem could be solved by doing EXAFS measurements.[ii] Hilbrandt et al. showed copper to occupy preferentially magnesium lattice sites (in a copper-doped magnesium oxide sample) with a comparative X-ray absorption near edge structure (XANES) study using various Cu-containing standards.

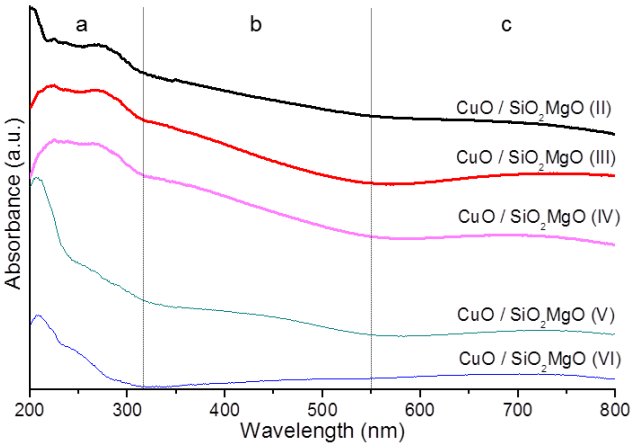

Figure 2. UV-Vis spectra of different $CuO/SiO_2/MgO$ catalysts, showing LMCT transitions in isolated CuO (a), LMCT transitions in cluster like CuO species (b) and d-d transition of octahedral Cu species (c).

In addition, the second goal of this research project is to study the catalyst in-situ under relevant reaction conditions. In particular, as H_2 is produced as part of the Lebedev process, changes can be expected in the oxidation state of the CuO promoter, thus leading to, at least partially, the formation of Cu(0) or Cu(I); EXAFS spectroscopy using a properly built cell to study the evolution of the catalyst is considered as the most suitable technique to study the speciation and coordination of Cu in our catalyst during reaction.[iii] Such a study of these catalyst systems and for this reaction has not been reported before.

Experimental technique, required set-up, measurement strategy, sample details (quantity, etc.):

A series of differently prepared CuO/SiO_2-MgO catalysts, showing large differences in catalytic activity, were previously characterized by TEM and UV-Vis methods and tested in the Lebedev conversion of bio-ethanol to 1,3-butadiene. Applying EXAFS we would like to study 4 catalysts with different activities.
The main objectives of this EXAFS study are: 1) the understanding of nature and speciation of the Cu species supported on SiO_2-MgO materials; and 2) register and understand the changes that occur in the catalyst during the reaction conducted at 698 K with a gas flow consisting of 2 mL/min EtOH and 98 mL/min N_2. Therefore, to study the catalyst materials under reaction conditions we will bring an in-situ cell previously used for in-situ EXAFS studies in our group.[iii] It is important to remark that the catalysts are nontoxic, air-stable and do not require any special preparation.

Beamline(s) and beam time requested with justification:

For set-up and measuring appropriate standards we will need 24 hours, preparing and conducting the in-situ experiments will take 3 days. A total of 4 days is sufficient for this study.

Results expected and their significance in the respective field of research:

We expect to:
- fully characterize the different CuO/SiO_2-MgO catalysts, gaining, in this way, a better understanding of the nature of supported Cu species and, as a consequence, of the reasons that lead to differences in activity for the catalysts prepared in different ways.
- understand changes in the speciation of Cu species exposed to the in-situ generated H_2 which could as a consequence lead to the deactivation of the catalysts with time-on-stream. We will bring and use a mass spectrometer for the detection of H_2 and other important reaction intermediates.

References

i C. Angelici, B. M. Weckhuysen, P. C. A. Bruijnincx, ChemSusChem 2013, **6**, 1595.
ii N. Hilbrandt, M. Martin, Journal of Physical Chemistry B 1999, **103**, 4797.
iii U. Deka, A. Juhin, E. A. Eilertsen, H. Emerich, M. A. Green, S. T. Korhonen, B. M. Weckhuysen, A. M. Beale, Journal of Physical Chemistry C 2012, **116**, 4809.