



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application**:

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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.



	Experiment title: Dynamical changes in methanol synthesis catalysts	Experiment number: CH-2591
Beamline: ID-26	Date of experiment: from: 07/05/2008 to: 13/05/2008	Date of report: 13/02/09
Shifts: 16	Local contact(s): Dr. Pieter GLATZEL	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Prof. Dr. W. Grünert, Dr. Van den Berg Maurits, O. Petrova*, A. De Toni*, Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, Universitätsstr. 150, D-44789 Bochum, Germany; Dr. Klementiev Konstantin, ALBA synchrotron light facility, Edifici Ciències Nord. Mòdul C-3 central., Campus Universitari de Bellaterra. Universita, 08193 Bellaterra, Barcelona, Spain; O. Tkachenko*, N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia		

Report:

Introduction

Interactions between the support and metal particle can critically modify catalytic properties in heterogeneous catalysis. With redox-active supports, metal and support form a dynamic system the state of which accommodates to the redox potential of the environment. The promoting action of the ZnO phase on the catalytic activity is still unclear under the real conditions of methanol synthesis [1-3]. Due to the low dispersion of ZnO in conventional methanol synthesis the evidence for promotion was mostly based on Cu spectra – where Zn spectra were involved, the effects were weak and questionable. We have now developed a model methanol synthesis catalyst in which a high dispersion has been imposed both on the Cu and on the ZnO particles by hosting them in a mesoporous siliceous matrix [4]. We could show that this catalyst is comparable with a technical methanol catalyst in terms of activity per copper surface area and that the Zn XAFS spectra exhibit significant changes indicating the appearance of Cu neighbours in the Zn coordination sphere [4] under conditions where strong interactions between Cu and ZnO are known to be favoured [5].

Some of our samples were inactive however, for reasons not well understood. A crucial step in the synthesis of the hosted samples is the slow and controlled hydrolysis of the zinc cubane precursor to a nano-crystalline zinc oxide phase. The mechanism of the hydrolysis could give us insight into the role of the support on the catalyst activity, which we suspected to be dependant on the formation of a nano-crystalline ZnO phase. We also investigated the effect of the calcination conditions of the as-made sample on the formation of the Cu and Zn phases, inspired by work of De Jong et al. [6]. They found that calcination of a nickel nitrate precursor in a stream of 1% NO can induce a higher dispersion of the metal through the reduction of its particle size, and we hypothesised that a similar effect could occur for our Cu/ZnO system.

Experimental

The measurements at the K-edge of Cu and Zn were carried out at ESRF beamline ID26 in transmission mode. For this the primary and transmitted intensity were measured by PIN diodes which detected scattering off thin glassy carbon (Sigradur TM) plates. The diodes were situated in the vertical plane i.e. perpendicular to the polarization of primary x-ray beam. Analysis of the XAFS spectra was performed with the software VIPER for Windows [8].

To study the hydrolysis at beamline ID-26 the precursor cubane solution in THF was contacted with a diluted water/THF solution in a custom-made reaction vessel. The kinetics of decomposition can be retarded by cooling the sample to 278 K, allowing the reaction to be monitored as it takes place by both XANES and EXAFS. Details of this procedure are described in [7].

The preparation of the matrix, which is a mesoporous silica of wormhole-type pore structure (average pore diameter 50 Å), as well as the subsequent loading with zinc cubane and copper (II) nitrate have been described in detail in [4,5]. Matrix-hosted samples were pre-treated and reacted in a plug-flow type cell, at various temperatures and atmospheres (see below), and subsequently exposed to a mixture of CO/H₂. Online mass spectrometry and infrared analysis of the process gas was used to establish the catalyst's activity.

Results

Our XAS studies at ID26 were instrumental to propose a detailed mechanism for the hydrolysis of the cubane precursor, which also takes

place inside the pores of the silica matrix (see figure 1). Water reacts with a Zn⁺-CH₃⁻ group, forming Zn-OH, which in turn polycondensates, forming Zn-O-Zn bridges, thus connecting the nanocrystalline ZnO building blocks.

The periods of nucleation and growth could be separately observed in the XANES of the reaction mixture: a clear double feature 9660 – 9675 at the start of the reaction transforms gradually to a structure very similar to ZnO.

In the EXAFS, the Zn-O shell is seen to increase during the hydrolysis, whereas the nanocrystalline character of the agglomerates is illustrated by the observed rapid amplitude decay in the final product.

These results, together with accompanying studies, have been published in [7].

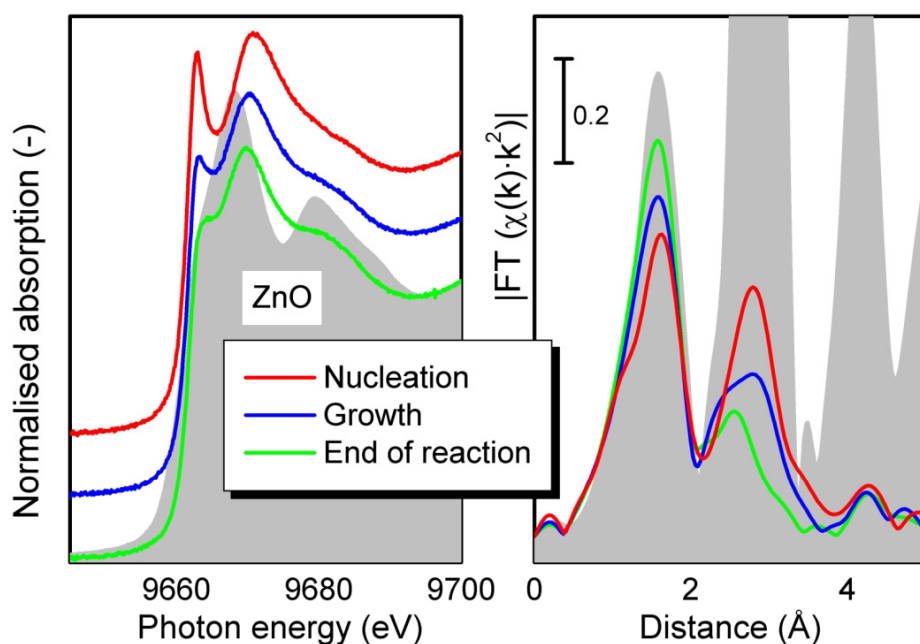


Figure 1: XANES (top left), EXAFS (top right) and proposed mechanism (bottom) for the formation of Zn-O building blocks from a zinc cubane precursor, with three distinguished stages nucleation, growth and end of reaction.

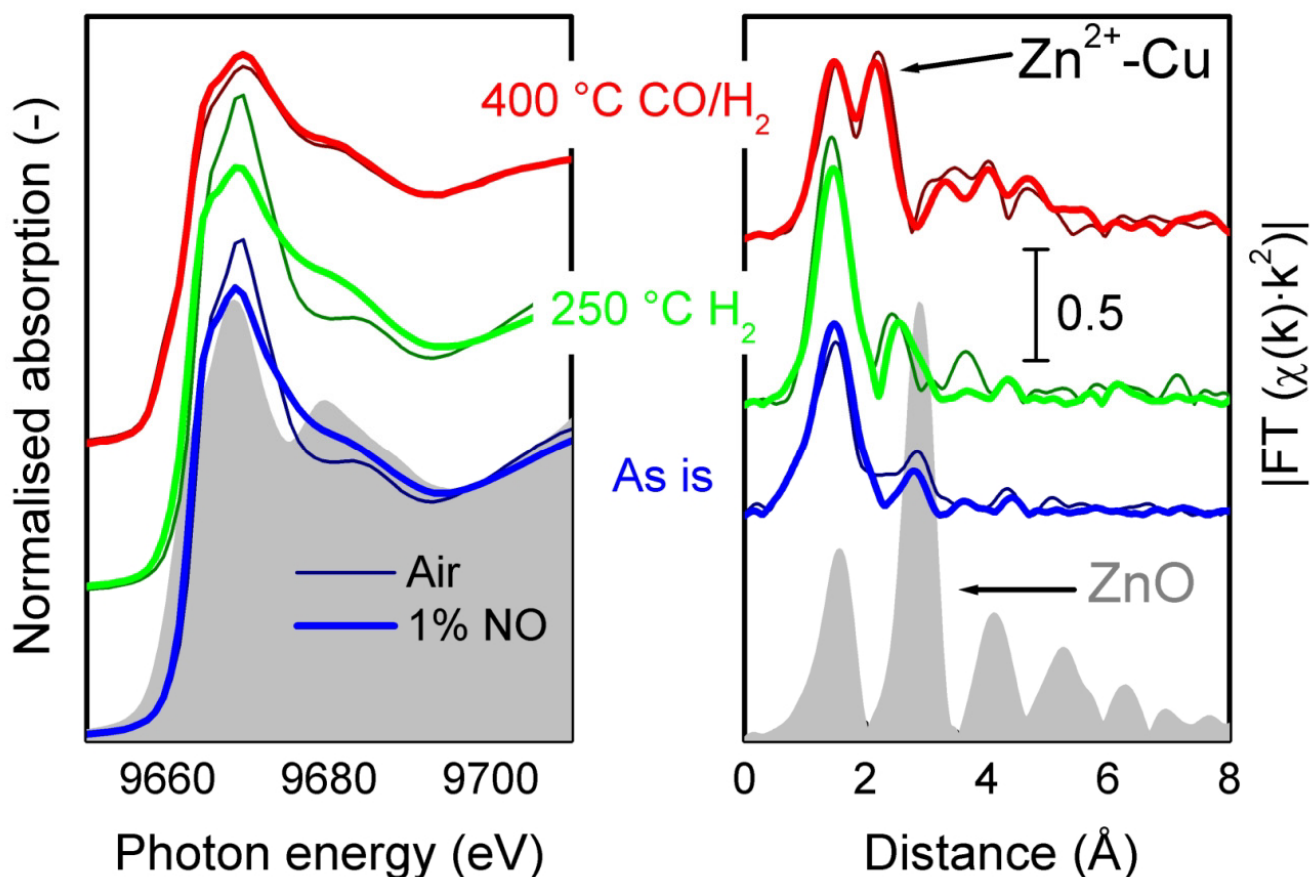


Figure 2: XANES (left) and EXAFS (right) of Cu/ZnO@WL-50, (23 % Zn, 4 % Cu) compared to bulk ZnO (shaded). Thick lines: sample calcined in 1%NO, thin lines: calcined in air. The Zn²⁺-Cu shell is indicated by an arrow.

The calcination of hosted ensembles in NO induced marked changes in their ZnO_x-phase compared to the air-calcined sample, as seen in the differences of the zinc white line, although the EXAFS are relatively similar (see figure 2). A temperature treatment at 250 °C in 5%H₂ did not lead to any reduction being observed at the Zn K-edge, but of course the copper was fully reduced (spectra not shown). At 400 °C in CO/H₂ (15 minutes hold), both the XANES and EXAFS of the NO and air-calcined sample are very similar indeed, with a very pronounced Zn-Cu shell of about the same height as the Zn-O shell. Contrary to expectations, in the copper spectra (not shown), no differences were seen between the two calcination procedures irrespective of the chosen temperature. Thus, although the history leading towards the active Cu/ZnO ensembles is clearly different between the two calcination procedures, under the chosen conditions the end product is the same, prompting the need for further fine-tuning of the sample pre-treatment to improve the copper dispersion.

In parallel measurements of the effluent methanol concentration, significant methanol formation was seen only on the catalyst sample depicted on Fig. 2, a companion sample where the Zn²⁺-Cu shell was missing remained completely inactive. This corresponds well with more accurate activity measurements in a laboratory setup [9] (conditions: 4 bar, 220 °C, CO/CO₂/H₂/He = 4/10/72/14 v/v%), where the methanol synthesis activity of this sample turned out to be in the same order of magnitude as that of a technical reference catalyst, with a distinct positive effect of a reductive pre-treatment (15 min CO/H₂, 400 °C as depicted in Fig. 2). While this observation clearly supports the crucial role of the Cu/Zn-interaction for methanol synthesis activity, the accuracy of the activity measurements at the ESRF station needs to be improved to clearly relate the formation of the Zn²⁺-Cu shell to extra activity proving thus its role as an active sites (instead of a spectator phenomenon). Therefore, more operando measurements will be clearly necessary. We will therefore submit a follow-up proposal, not before 2010, however, to allow for a solution of experimental problems mentioned (reproducibility of the catalyst synthesis to be improved by controlling the Zn heterocubane hydrolysis conditions, fine-tuning of the drying and calcination pre-treatment for maximisation of the Cu dispersion).

References

1. B. S. Clausen, J. Schiøtz, L. Grabaek, C. V. Ovesen, K. W. Jacobsen, J. K. Nørskov, H. Topsøe, *Top. Catal.* 1:367 (1994).
2. J.-D. Grunwaldt, A.M. Molenbroek, N.-Y. Topsøe, H. Topsøe, B.S. Clausen, *J. Catal.* 194:452 (2000)
3. M. M. Günter, T. Ressler, R. E. Jentoft, B. Bems, *J. Catal.* 203: 133 (2001).
4. a) M. W. E. van den Berg, S. Polarz, O. P. Tkachenko, K. V. Klementiev, M. Bandyopadhyay, L. Khodeir, H. Gies, M. Muhler, W. Grünert, *J. Catal.* 241:446 (2006), b) Berg, M. W. E.; Polarz, S.; Tkachenko, O. P.; Kaehler, K.; Muhler, M.; Gruenert, W., *Catalysis Letters* 128:49 (2008)
5. S. Polarz, F. Neues, M. W. E. van den Berg, W. Grünert, L. Khodeir, *J. Am. Chem. Soc.* 127:12028 (2005).
6. Sietsma, J.R.A., Friedrich, H., Broersma, A., Versluijs-Helder, M., van Dillen, A. J., de Jongh, P.E., de Jong, K.P., *Journal of Catalysis* 260(2): 227 (2008)
7. Lizandara-Pueyo, C.; van den Berg, M. W. E.; De Toni, A.; Goes, T.; Polarz, S. , *J. Am. Chem. Soc.*, 130: 16601(2008)
8. K.V.Klementiev, VIPER for Windows, freeware, www.desy.de/~klmn/viper.html
9. I. Ellmers, Bachelor thesis, Laboratory for industrial Chemistry, Ruhr University Bochum, Bochum (2008).