



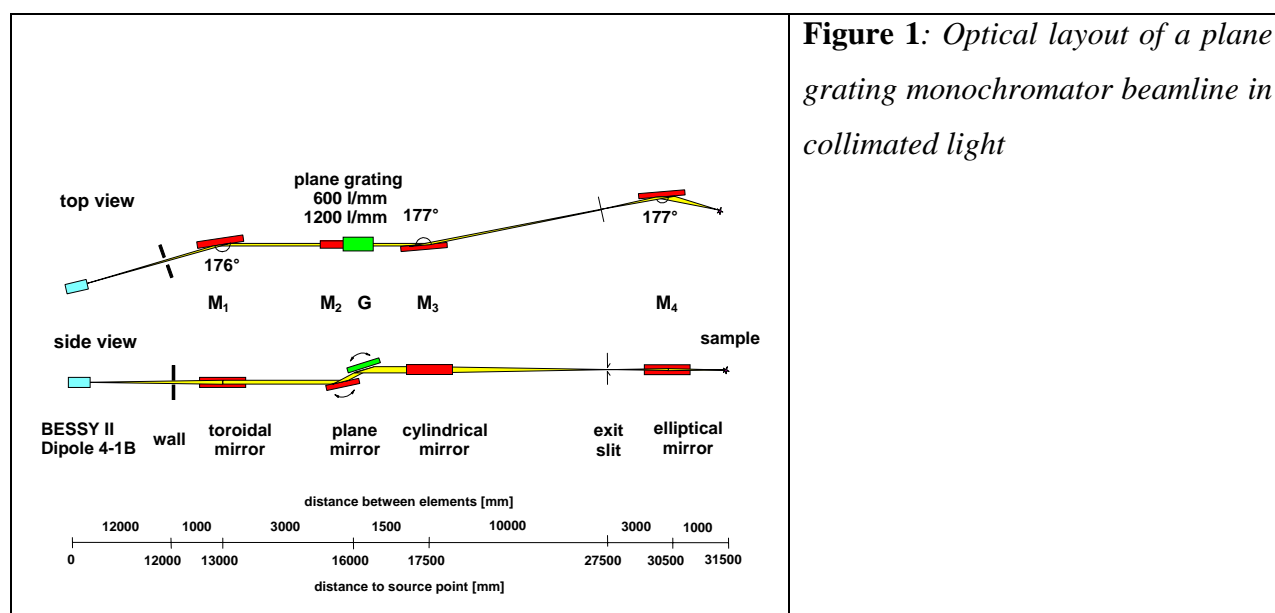
## *In situ* XPS at a bending magnet beamline: Study of the electronic structure of binary Cu/Zn catalysts

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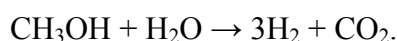
### Introduction

*In situ* X-ray photoelectron spectroscopy is a powerful tool for the investigation of dynamic processes studied in the field of material science and catalysis. Several examples of the application of this technique can be found in this and previous annual reports. The study of a catalyst under working conditions often requires a complex gas feed and an elaborated gas analytic to follow the conversion of the gas phase during the reaction. It might be frequently unavoidable to use hazardous substances (e.g. poisonous or flammable) as reactants. It is obvious that a permanent endstation at a beamline dedicated for spectroscopic *in situ* investigations can fulfill these requirements much more efficiently than a non-permanent installation. A broad range of spectroscopic investigations should be performed at this beamline. An optical setup based on a plane grating monochromator (PGM) working in the collimated light is most suitable because the operation of the beamline can be optimized for the specific needs of the users without any hardware modifications (e.g. setting of slit positions, mirrors). A schematic view of the proposed optical layout can be found in Fig. 1.



The Russian-German beamline (RGLB) operated at a BESSY bending magnet is based on a PGM working in collimated light [1]. Therefore, we used RGLB to test the opportunity for *in situ* XPS investigation at a bending magnet beamline in general, although this beamline is not optimized for operation with the already existing *in situ* XPS endstation.

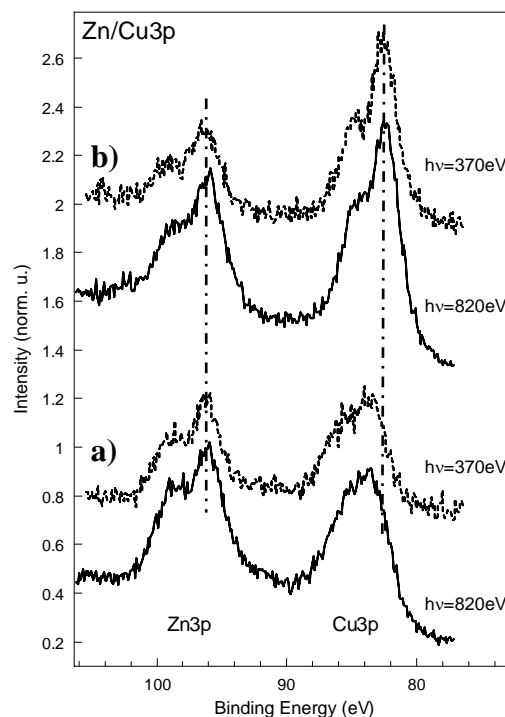
Cu/ZnO (alumina) catalysts are common catalysts for the hydrogenation of carbon monoxide and carbon dioxide. These systems have found industrial use for the low-temperature methanol synthesis, for the low-temperature water-gas shift reaction, and for the steam reforming of methanol following the reaction [2]:



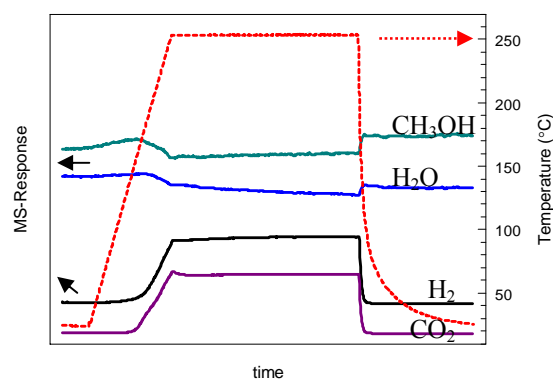
An important application could be the onboard production of hydrogen for fuel cell application. It is the proposed synergistic effect in the binary copper/zinc oxide that makes this system interesting for investigation [3-5]. The maximum activity is obtained in an intermediate compositional range, whereas Cu and ZnO alone exhibit only negligible activity [6].

## Results and discussion

Fig. 2 shows *in situ* XP spectra of a Cu/ZnO catalyst in 1 mbar  $\text{H}_2$ . The lower set of spectra (a) shows the catalyst before the activation at room temperature and the upper set (b) was taken during the activation process in hydrogen at 250°C. Spectra with two photon energies resulting in different information depths were taken at each condition. The shift of the Cu3p core level indicates a reduction of Cu but not of Zn. It can be seen that during the activation the catalyst surface got enriched with copper. Furthermore, this ex-



**Figure 2:** Zn3p and Cu3p core level spectra. The spectra were taken at 1 mbar  $\text{H}_2$  before the activation at room temperature (a) and during the activation at 250 °C (b). The incidence photon energy was varied as indicated.



**Figure 3:** Mass spectrometer response while the catalyst was heated in a mixture of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  were consumed and  $\text{H}_2$  and  $\text{CO}_2$  evolved at the same time.

ample shows a nice application of the depth-profiling technique by variation of the incident photon energy. A gradient of the Cu/Zn ratio was found by this technique with the higher Cu concentration at the outermost surface under this activation conditions. After the activation in hydrogen the sample was heated in a 1:1 mixture of methanol and water ( $p_{\text{tot}}=0.25$  mbar). The mass spectrometer response during the reaction is shown in Fig. 3. It can be seen by the consumption of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  and the evolution of  $\text{H}_2$  and  $\text{CO}_2$  at the same time that the activated catalyst presented in Fig. 2 is active in the methanol steam reforming reaction.

These results demonstrate that it is feasible to carry out successfully *in situ* XPS measurements at a PGM bending magnet beamline. It should be noted that a beamline specially designed for operation with the *in situ* XPS setup is expected to result in an even better performance.

### Acknowledgement

The authors want to acknowledge Denis Vyalikh and Rolf Follath for their assistance during the beamtime at the Russian German Beamline. MH gratefully acknowledges Fred Senf for support and valuable discussions concerning beamline layouts.

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