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### Understanding the activity of Zn-Cu sites in methanol synthesis

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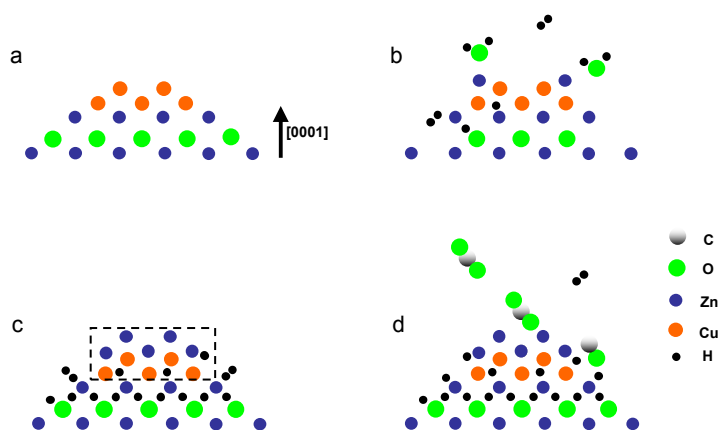
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## Summary

This thesis deals with the Cu/ZnO interaction in activated methanol synthesis catalysts. A combination of classical characterization techniques and surface science techniques was applied to probe the dynamic modification of catalyst structure upon the activation in hydrogen. Based on the findings described in the thesis, the active sites of the Cu/ZnO methanol catalysts consist of the Zn-Cu alloy sites (Fig. 1) that are completely formed after reduction at 800 K. Apart from creating active sites, ZnO plays an important role in methanol synthesis as an atomic hydrogen supplier. ZnO bulk acts as a hydrogen reservoir for the reaction. The hydrogen was absorbed by ZnO matrix during the reduction treatment. The stored atomic hydrogen already releases at temperatures of 500 K and became available for the reaction at the industrial conditions of 520 K. The metallisation of ZnO surface by Zn upon the reduction boosts dissociative adsorption of  $H_2$  from the gas phase at temperatures above 500 K. Copper plays a promoting role in this metallisation.



**Fig. 1.** Scheme of the Cu/ZnO transformation towards Cu clusters coated by Zn: a) Cu cluster deposited on clean ZnO(0001)-Zn face decorated by O at the step edges; b) reduction process at 700 K - the surface is enriched by Zn and oxygen is removed as a water; c) an activated state of Cu/ZnO surface alloy is formed denoted with dashed line ( $Zn(OH)_2$  is not shown); d) adsorption of  $CO/CO_2$  with O downwards on the Zn-Cu sites.

Finally, after reduction at 800 K, this interaction delivers the highest active surface area of Zn-Cu sites on top of the immobilized Cu platelets of about 5 nm in average, that are homogeneously spread over the ZnO surface. The active structure is resistant to the elevated temperatures of about 800 K. Moreover, the stable Zn-Cu alloy structure on top of the ZnO strongly suggests that no re-activation treatment is required. Therefore the current low pressure methanol synthesis could be used even more efficiently.