Theoretical Study on Molecular Models for ZnO Catalysts

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The formation of methanol from synthesis gas by heterogeneous catalysis at ZnO based catalysts is one of the most important processes in industrial chemistry. In the last years, there is a renewed interest in a detailed understanding of the reaction mechanism. In addition to studies on real catalysts and on clean ZnO surfaces under UHV conditions a third possibility to get insight into the catalytic process is the synthesis and investigation of molecular models for ZnO. Driess et al. synthesized different alkoxy zinc hydrides, namely $(MeZn)(H\text{-}Zn)_3(O^tBu)_4$ and $(thf{\bullet}Li)(H\text{-}Zn)_3(O^tBu)_4$, and investigated the reaction of these compounds with CO and CO_2. It was found experimentally, that CO_2, but not CO, can be inserted into the Zn-H bonds and the reaction was traced by in situ IR spectroscopy.

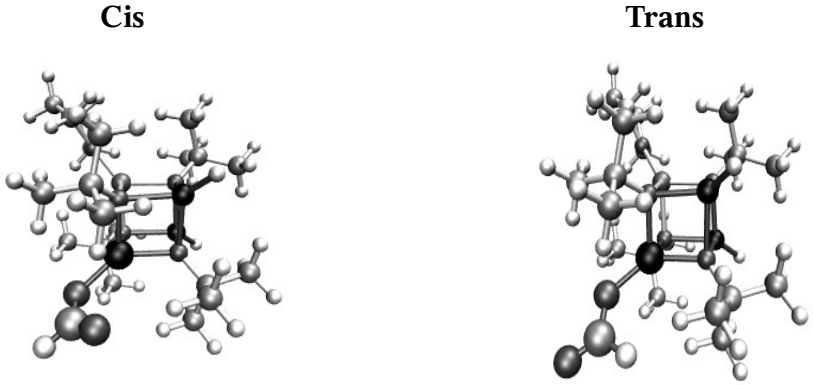

Figure 1: CO_2 insertion into a Zn-H bond of $(thf{\bullet}Li)(H\text{-}Zn)_3(O^tBu)_4$ alkoxy zinc hydride

In this work, we performed quantum chemical calculations on the alkoxy zinc hydrides and on the products of CO and CO_2 insertion. We optimized the structures, and calculated the binding energies and vibrational frequencies. For all calculations the program package TURBOMOLE 5.6 was used. The results were obtained by RI-DFT calculations using the BP86 functional and TZVP basis sets. For binding energies zero point vibrations were included.

The results can be summarized as follows: While the calculated binding energy of CO is close to zero (0.04 eV), we found two different structures for CO_2 insertion (see fig. 1) with binding energies in the range of 0.2 to 0.5 eV. For both alkoxy zinc hydrides the cis structure is stabler. The binding energy is about 0.1 eV higher for the experimentally more reactive Li compound. Comparison of the measured and calculated CO stretching frequencies implies that the cis as well as the trans structure are observed in experiment.

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