

Au/ZnO and ZnO catalysts in methanol synthesis: A steady state, transient kinetic and DRIFTS study

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Introduction

Several models for methanol synthesis on ZnO are under discussion, assuming oxygen vacancies on polar ZnO surfaces as active sites for the hydrogenation of CO [1] or CO₂ [2] to methanol. It has been shown that Au can be an active catalyst in CH₃OH synthesis, when it is well dispersed in small nanoparticles on oxidic supports, and ZnO was shown to be essential to obtain high selectivity towards CH₃OH [3]. *In situ* DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) was applied to identify adsorbed surface intermediates, steady state kinetic experiments gave insight in reactivities and transient kinetic experiments were used to monitor single elementary steps and to investigate reaction pathways.

Materials and Methods

Au/ZnO samples were prepared by the colloidal deposition method [4]. An all stainless steel microreactor set-up was used in this study containing a glass-lined stainless steel U-tube reactor, a back pressure regulator and a quadrupole mass spectrometer. For DRIFTS studies the set-up is equipped with a Nicolet Nexus FTIR-spectrometer. CH₃OH adsorption experiments on ZnO and 1 wt% Au/ZnO were performed two times, that is, as TPSR (temperature-programmed surface reaction) experiment in the U-tube reactor and in the DRIFTS cell to investigate the intermediates adsorbed on the surface. Activity was measured in CO₂-free and CO₂-containing synthesis gas under varying conditions (25-40 bar; 523-573 K) until steady state was reached. Subsequently, reactive frontal chromatography (RFC) with N₂O was performed.

Results and Discussion

Two different methoxy species are developing during methanol adsorption, differing in the surface-sensitive IR bands of the C-O stretching vibration and their decomposition temperature to formate [5]. Two H₂ desorption peaks were observed without any other desorbing species in the TPSR experiment (Fig. 1). Two different formates result from the methoxy decomposition, which differ in the IR-bands of the OCO-stretching vibrations. The TPSR peaks originating from their decomposition are widely overlapping, so that a separation is not possible. A peak and a shoulder of H₂, together with CO and CO₂ desorption, were assigned to the decomposition of the two formed formate species (Fig. 1). Based on the disappearance of OH groups on different single crystal surfaces of ZnO during methanol adsorption and on the different reactivities of polar and non-polar surfaces of ZnO in methanol synthesis, the different adsorbates are assigned to be located on either ZnO(10-10) or ZnO(000-1). Based on the heating rate variation method, activation energies of the methoxy decomposition to formate are found to be 109 kJ mol⁻¹ (ZnO(000-1)) and 127 kJ mol⁻¹ (ZnO(10-10)). Also on Au/ZnO methoxy and formate species are found when performing these

experiments, but more CO₂ is produced during the TPSR experiments, presumably due to the formation of oxygen vacancies. CH₃OH exposure causes an increase in the absorbance due to reduction of the surface [6]. Thus, Au enhances the reducibility of ZnO.

In the activity tests all Au/ZnO samples are more active than pure ZnO [4]. The amount of N₂ formed during RFC experiments with N₂O is in good agreement with the amount of removable lattice oxygen derived from reduction-oxidation processes in a static microcalorimeter using CO and O₂. The amount of vacancies titrated by N₂O correlate with the number of Au perimeter atoms present in the Au/ZnO catalysts suggesting an enhanced formation of oxygen vacancies at the Au/ZnO interface. In both synthesis gas mixtures Au particles lead to an increased activity compared with pure ZnO. All Au/ZnO samples exhibit higher catalytic activity in the absence of CO₂, as has been observed for pure ZnO. It is concluded that oxygen vacancies in ZnO are also the active sites in CH₃OH synthesis over Au/ZnO, and that the presence of the Au enhances the number of exposed oxygen vacancies in ZnO, presumably located in the interface region.

Significance

CH₃OH is one of the promising candidates as a future fuel. CH₃OH synthesis catalysts of industrial relevance have always contained ZnO. Nowadays, ternary Cu/ZnO/Al₂O₃ catalysts are used. It has been postulated that highly active sites at the interface between Cu and ZnO play an important role [7-9]. However, pure ZnO and Au/ZnO can also be an active for CH₃OH synthesis, and it is desirable to understand their performance in CH₃OH synthesis.

References

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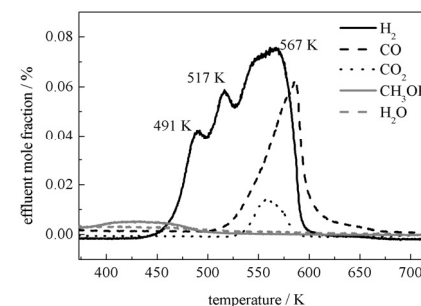


Figure 1. Methanol TPSR on ZnO powder.