Heterogeneous Catalysis

Active Sites on Oxide Surfaces: ZnO-Catalyzed Synthesis of Methanol from CO and H_2**

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Chemical processes on metal oxide surfaces have been of great interest for a long time, mostly due to their relevance in the field of heterogeneous catalysis. Since “perfect” oxide surfaces usually show only little or no activity, it is widely believed that the high reactivity of oxide powders results from the presence of a small number of active sites.[1] Most of the models proposed for these active sites are based on oxygen vacancies or defects. There is literature consensus on the role of these active sites and the particular importance of oxygen vacancies. However, only a few case studies have been described in which for a specific reaction the geometric structure of an active site is not only specified, but also confirmed by theoretical calculations and validated by kinetic studies conducted in a reactor under conditions close to those applied industrially.

We have conducted such a study for the synthesis of methanol over ZnO powders. In a recently published theoretical paper,[2] an active site and a reaction mechanism were proposed but without a comparison to kinetic data. It was assumed that a Cu-free model for the active site is sufficient to explain the formation of methanol from a CO_2/H_2 mixture on an industrially applied $Cu/ZnO/Al_2O_3$ catalyst. In our extensive analysis we find—for an active site similar to that proposed—an energetically more favorable reaction pathway, in which it is not carbon dioxide acting as carbon source, as was assumed so far, but carbon monoxide, which is favored for thermodynamic reasons. On the ZnO-supported Cu-containing powder catalysts used at present for the industrial synthesis of methanol, another reaction mechanism with carbon dioxide as the carbon source is occurring. This was a point of controversy for a long time, but the mechanism

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[**] This research was supported by the German Science Foundation within the framework of the Collaborative Research Center 558 “Metal–Substrate Interactions in Heterogeneous Catalysis”.

DOI: 10.1002/anie.200462374

was finally clarified by experiments using isotope-labeled reactants.[3–7]

One of the major problems in the analysis of chemical processes on such active sites is their typically rather low concentration on the surface. Thus, the systematic analysis of precise data by the well-established methods of surface physics and chemistry is impossible or at least highly problematic. For example, it is not possible to determine experimentally the binding energy of CO on defect sites with reliability. Just recently, reliable information available concerning binding energies on perfect ZnO surfaces was reported.[8–11] In the present study, we have therefore chosen an approach in which we combine precise quantum chemical ab initio calculations—which had been validated beforehand by calculations on perfect systems and by a comparison with experimental data[12]—with detailed measurements under steady-state conditions close to those applied in industry. Based on these measurements and the quantum chemical results, we propose a reaction mechanism in which a CO molecule is bound in an unusual adsorption geometry and transformed into a formyl species.

The kinetic and characterization studies of several differently prepared ZnO powder samples presented in ref. [13] showed that methanol synthesis on ZnO is a structure-sensitive reaction; polar surfaces are distinguished by their high turnover frequencies. Figure 1 compares reactions performed with a Cu-free binary ZnO/Al_2O_3 catalyst and a ternary Cu catalyst under near-industrial reaction conditions. The latter catalyst is applied technically in large-scale, low-temperature methanol synthesis. Under similar conditions it is much more active than the binary ZnO/Al_2O_3 catalyst, which is highly temperature-stable. When a CO/H_2 mixture is used, the space–time yield (STY) is already on the same order of magnitude as when the temperature is 100 K lower. The difference in the STYs is even more pronounced when gas mixture with another composition is employed. A synthesis gas containing CO_2 results in a drastic increase in activity for the ternary system but a decrease for the binary system.

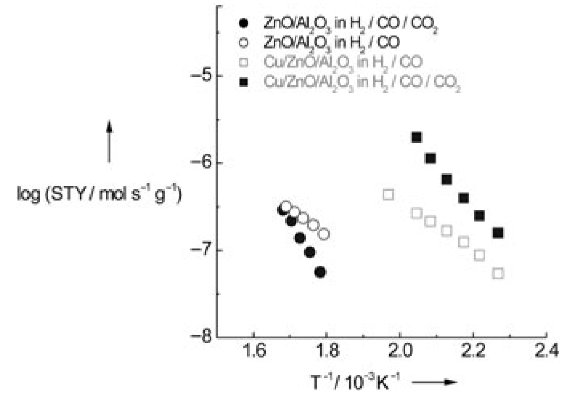

Figure 1. Comparison of the activity of the binary and ternary catalysts.

The inhibiting effect of CO_2 was proven by the following experimental sequence: a gas mixture containing about 72% H_2, 10% CO, and 18% N_2 was passed over the ZnO/Al_2O_3 catalyst at a flow rate of 100 NmL min^{-1}. When the CH_3OH concentration was constant over time, 1% CO_2 was added to the synthesis gas. The concentrations of CO and H_2 were kept constant, and only the N_2 content was adjusted. After the system had again reached a steady-state CH_3OH content, the CO_2 fraction in the inlet flow was increased to 2, 3, 4, 6, and 8%. The activity plot thus determined experimentally (Figure 2) clearly shows that even an addition of CO_2 as low as 1% results in a strong decrease of the CH_3OH yield. Further addition of CO_2 continuously lowers the CH_3OH yield, but the effect is less pronounced. CO_2 therefore seems to act on the ZnO/Al_2O_3 catalyst as a catalyst poison. Since the catalytic activity of the ZnO/Al_2O_3 catalyst depends on the preset CO/CO_2 ratio, the working state of the active site under industrial conditions is of particular importance.

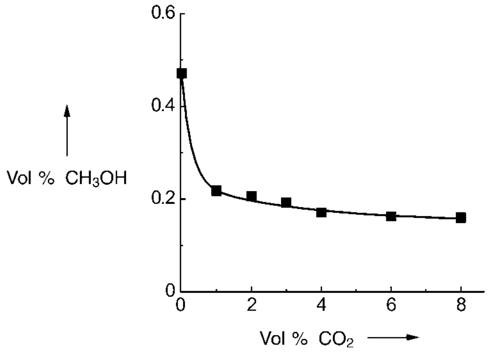

Figure 2. The activity of the coprecipitated ZnO/Al_2O_3 catalyst as a function of the fraction of CO_2 in the inlet flow. Experimental conditions: $\dot{V}$ = 100 NmL min^{-1}, T = 583 K, P = 4.1 MPa, $w_{cat.}$ = 1.00 g.

Even small amounts of CO_2 in the synthesis gas markedly lower the formation of CH_3OH on the ZnO/Al_2O_3 catalyst. This observation strongly supports the hypothesis that the active site of the ZnO/Al_2O_3 catalyst is an oxygen vacancy. In this case the number of active sites on the catalyst would increase in a highly reducing atmosphere (no CO_2, high level of CO). Supplementary measurements confirmed the formation of small amounts of CO_2 when the catalyst was exposed to a gas mixture with a high concentration of CO. These findings can be explained by a direct removal of oxygen from the ZnO lattice by CO, leading to the formation of CO_2. Inversely, addition of CO_2 to the synthesis gas would cause an oxidation of the vacancies and catalyst activity would drop.

To support these mechanistic ideas we performed quantum chemical ab initio calculations to determine the geometric structure and the energies of different intermediates for the reaction of CO with 2 H_2 over ZnO catalysts. An "embedded cluster" approach was used in which the surroundings of the active site are described by a cluster treated explicitly with quantum chemical methods while the cluster itself is embedded in an extended point-charge field.

As in the work of French et al.,[2] the polar O-terminated ZnO$(000\bar{1})$ surface was chosen as starting point for our calculations. To build a model for the active center we first investigated the atomic structure and chemical composition of the $(000\bar{1})$ surface under catalytic conditions. For a long time it was believed that the $(000\bar{1})$ surface of ZnO is unreconstructed and exhibits an ideal "truncated bulk" structure. Because of the polar character of the $(000\bar{1})$ surface inevitably partly occupied surface bands would be present in this case, leading to a vanishing band gap.[14,15] However, in the last years it was shown by experimental and theoretical work[11,12,16] that the $(000\bar{1})$ surface is stabilized by the formation of O vacancies or the adsorption of hydrogen, depending on the experimental conditions. The driving force behind these structural changes is the avoidance of partly filled surface bands. Assuming that the $ZnO(000\bar{1})$ surface is in thermodynamic equilibrium with H_2 and O_2 in the gas phase, Meyer[16] determined a surface phase diagram by using DFT slab calculations. At pressures and temperatures typically employed in methanol synthesis the most stable structure was found to be a surface with a hydrogen-atom surface coverage of 50% where all surface bands are filled.

The point-charge field used for the embedding of the ab initio cluster was generated by using the optimized structure of the hydroxylated $ZnO(000\bar{1})$ surface from ref. [16]. The active site with the O vacancy was obtained by removing an entire H_2O molecule from the surface in accordance with the tendency to avoid occupied surface states (Figure 3). As the first step, the adsorption geometries for different adsorbed intermediates were determined.[17] All atoms of the adsorbates and the positions of the three Zn ions together with the six surface O atoms (including the H atoms bound to these O atoms) next to the vacancy were relaxed. For the optimized structures the adsorption energies were calculated with the Bochum program package,[18–20] taking into account the dynamic correlation within the multiconfiguration coupled electron pair approximation (MCCEPA),[20] an approximate coupled-cluster method. We used TZVPP basis sets for the adsorbate molecules and the Zn and O ions of the first coordination shell of the active site. The basis set superposition error for the binding energy was corrected as proposed by Boys and Bernadi.[21] To compare the energies of the different intermediates it is important to correct all energies for zero-point vibrations, since they change dramatically during the reaction: for the gas-phase reaction $CO + 2H_2 \rightarrow CH_3OH$, by 64.7 kJ mol^{-1} (for experimental data see ref. [22]).

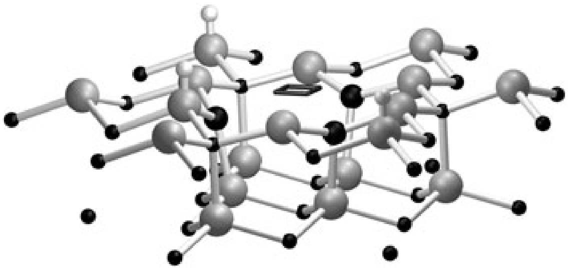

Figure 3. The ab initio cluster consists of the three Zn atoms of the first Zn coordination shell (black, big) next to the defect site (square), the nine O atoms of the first O coordination shell (six from the first and three from the second layer, gray), three O atoms from the third layer that are a short distance (4.567 Å) from the defect site, six further O atoms from the first layer (gray), all H atoms (white) bound to the cluster O atoms, and of all Zn atoms neighboring the cluster oxygen atoms (black, small).

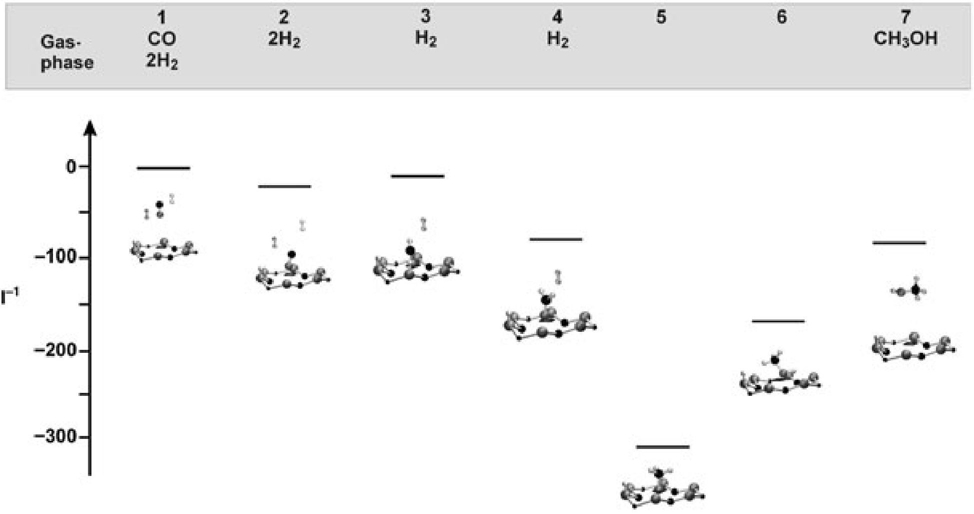

Figure 4. Potential energy diagram and adsorption geometries for formation of methanol from CO and H_2 catalyzed by ZnO. Cluster: Zn black, O gray, H white; Adsorbate: C black, O gray, H white.

Figure 4 shows the geometries and the relative energies of the most important steps in the reaction mechanism for the synthesis of CH_3OH from CO and H_2. The binding energies for the optimized structures are given in Table 1.

The combination of the results of the quantum chemical calculations and the kinetic measurements suggests the following model for the overall reaction: Over ZnO catalysts, methanol is formed mainly from adsorbed CO. At the active site CO is adsorbed perpendicularly to the surface and can be bound either through the C or the O atom. The binding energy for the C-bound configuration, 17.1 kJ mol^{-1}, is almost the same as for the O-bound adsorption within the accuracy of the calculations. Therefore, both situations should be present under catalytic conditions. CO adsorbed through the oxygen atom is more favorable for the subsequent hydrogenation steps. Hence, this configuration was considered in our calculations for the next steps. The calculated binding

Table 1: Calculated energies [kJ mol^{-1}] of the intermediates relative to the energy of the starting compounds.

	Adsorbate(s)	Gas phase	ΔE(SCF)	ΔE(MCCEPA)	NPE [a]	E incl. NPE	d_O [Å][b]
1		$CO+2H_2$	0.0	0.0	66.2	0.0	
2	OC	$2H_2$	−12.0	−15.0	66.2	−15.0	0.90
3	CHO^-, H^+	H_2	3.4	3.1	61.5	−1.6	0.22
4	CH_2O	H_2	−91.2	−105.8	96.0	−76.0	0.53
5	CH_3O^-, H^+		−320.0	−344.0	102.6	−307.6	0.12
6	CH_3OH		−193.0	−226.1	134.2	−158.1	0.79
7		CH_3OH	−115.1	−143.7	134.2	−75.8	

[a] NPE: calculated zero-point energy. [b] d_O: distance of the O atoms from the position of the defect site.

energy for CO at the active site is much smaller than the CO_2 adsorption energy of 69.0 kJ mol^{-1} obtained by French et al.[2] Therefore, CO_2 in the synthesis gas can possibly block the active site for the CO reaction.

We expect the formation of a formyl species to be the next reaction step.[24–27] It is well known that H_2 adsorbs dissociatively at the O vacancies of the polar surfaces. Therefore, we assume that formyl is formed by the transfer of H^- to the carbon atom of the CO, adsorbed through the oxygen atom, at the active site, while a neighboring oxygen atom is protonated at the same time. In the energy diagram in Figure 4, the formyl species has about the same energy as the starting situation as a result of two compensating effects: The adsorption of the negatively charged formyl species is strongly stabilized in the Madelung field of the ZnO environment and leads in combination with the proton affinity of the cluster to strong binding at the active site. On the other hand, breaking the CO triple bond and dissociating the H_2 molecule cost a lot of energy.

Since the adsorption of CO on ZnO is weak,[12,29] we assume that the formation of formyl is the rate-determining step in methanol synthesis. The following stepwise hydrogenation of the formyl species with dissociatively adsorbed hydrogen leads to the methoxy species, which is also observed on ZnO in studies on intermediates.[27,30–32] The formyl species abstracts the proton of a neighboring OH group, rearranges to formaldehyde, and then reacts with a further H^- to give the strongly bound methoxy species. The methoxy ion is adsorbed such that the negatively charged oxygen atom is located at the defect site. In the last hydrogenation step, a proton of a neighboring OH group is transferred to the methoxy species forming methanol. The methanol molecule desorbs from the surface, the O defect is reestablished, and the catalytic cycle is completed. The catalyst is regenerated continuously, since in the presence of CO and H_2 at high temperatures small amounts of CO_2 and H_2O are always formed, leading to the formation of new active sites. This might be the reason why ZnO is very stable under reaction conditions and suitable as a catalyst for CO hydrogenation under industrial conditions.

Adding CO_2 to the CO/H_2 gas mixture leads to a change in the reaction mechanism in the ZnO-catalyzed methanol synthesis. In analogy to the mechanism described in ref. [2] for ZnO or to the redox mechanism postulated for Cu-containing catalysts,[33] the reaction path for the hydrogenation of CO_2 includes the formation of a formate and a methoxy species as intermediates. In the presence of CO_2, the formation of methanol is significantly slower. In contrast to the CO mechanism via a formyl species, the reaction path with CO_2 takes place preferentially under these reaction conditions because the formate intermediate is more stable than formyl. In our opinion, the activity of the Cu-containing catalyst is determined by the strong interaction between Cu and ZnO_{1-x} (x is equal to the number of O vacancies). The hydrogenation of CO_2 at the Cu-ZnO_{1-x} interface is favored over the conversion of CO.[34] For definite proof that methanol is formed by these two different reaction paths, spectroscopic analysis of the intermediates, calculation of transition states, and comparison of the results obtained by microkinetic modeling based on quantum chemical calculations with the data of kinetic measurements will be necessary.

Experimental Section

The catalysts were synthesized by the coprecipitation method. The hydroxycarbonate precursors were prepared by precipitation from metal nitrate solutions with sodium carbonate at pH 7. The concentrations of the nitrate solutions was adjusted to a nominal catalyst composition of 85 mol% ZnO and 15 mol% Al_2O_3 for the ZnO/Al_2O_3 catalyst. The resulting precipitate was aged in the mother liquor under continuous stirring for 2 h. The aged precipitate was filtered and washed with deionized water (6 × 20 mL). Drying was performed overnight at 393 K followed by calcination in synthetic air ($\dot{V} = 10$ NmL min^{-1}) increasing the temperature from room temperature to 593 K at a heating rate of 2 K min^{-1} and maintaining the temperature for 3 h. The calcined precursor was pressed and sieved, yielding a grain fraction of 250–355 μm. The preparation of the ternary Cu/ZnO/Al_2O_3 catalyst with a nominal catalyst composition of 70 mol% Cu, 15 mol% ZnO, and 15 mol% Al_2O_3 followed the same procedure.

For the catalytic experiments, 1.00 g of the calcined precursor (250–355 μm) was used in a fixed-bed single-pass tubular reactor (bed length ca. 2.1 cm). For pretreatment, the sample was heated at a constant rate of 1 K min^{-1} to 448 K and held at this temperature overnight. A mixture of 2% H_2 in He ($\dot{V} = 60$ NmL min^{-1}) was chosen as the pretreatment gas. Then the reactor temperature was increased at a constant rate of 1 K min^{-1} to 513 K and held at this temperature for 30 min. Then the pretreatment gas mixture was replaced with pure hydrogen ($\dot{V} = 60$ NmL min^{-1}). The space-time yield (STY) was determined at 4.1 MPa and 453–583 K using synthesis gas mixtures containing H_2, CO, CO_2, and N_2 with the following composition: (○) 73.1% H_2, 10.8% CO, 16.1% N_2; (●) 72.3% H_2, 9.9% CO, 4.5% CO_2, 13.3% N_2; (□) 73.9% H_2 9.6% CO, 16.5% N_2; (■) 73.2% H_2, 9.5% CO, 4.6% CO_2, 12.7% N_2.

Received: October 20, 2004
Revised: January 18, 2005

Keywords: heterogeneous catalysis · kinetics · methanol synthesis · quantum chemistry · zinc oxide

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