Understanding the activity of Zn-Cu sites in methanol synthesis

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Chapter 6

Exploring the activated state of Cu/ZnO (0001)-Zn, a model catalyst for methanol synthesis*

Abstract

The interaction of Cu clusters with ZnO (0001)-Zn terminated crystal faces is studied after reduction at high temperatures by a combination of scanning tunnelling microscopy, scanning tunnelling spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermal desorption spectroscopy. We find that tiny amounts of Cu promote the reduction of the ZnO surface by means of triangular reconstruction. This metallisation of the surface leads to a Cu-Zn alloy. The XPS results reveal that the degree of alloying depends strongly on the reduction temperature. This alloying stabilises Zn from evaporation and H2 desorption below 500 K. On basis of these results, we conclude that the activated catalyst surface consists of Zn-Cu alloy sites that form at 700-800 K. Moreover, the surface alloying enhances the activity of Cu/ZnO catalysts under typical methanol synthesis conditions.

6.1 Introduction

Copper/zinc oxide based catalysts are used worldwide for methanol synthesis (1), methanol steam reforming (2) and water-gas

shift reactions (3) [1-4]. These are very large-scale processes (methanol production alone accounts for 75 million tpa of metric tons per annum [5, 6]). Remarkably, the combination copper/zinc oxide has unique chemical properties, that are absent from its individual components. For example, both polycrystalline copper powder and copper single crystals show only minimal methanol synthesis activity compared to Cu/ZnO [7]. Similarly, the activity of ZnO single crystals is marginal [8]. This shows that methanol synthesis is catalysed by active sites which are formed by an interaction between Cu and ZnO [4, 9]. The problem is that we still don’t understand the nature and mechanism of the active sites. This understanding is crucial for optimising these catalytic processes.

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\begin{align*}
\text{CO} + 2\text{H}_2 & \rightarrow \text{CH}_3\text{OH} \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

There are different opinions in the literature about the active site. These may be classified as: i) Cu\(^+\) [4]; ii) dynamic Cu particles [11]; iii) wetting-nonwetting of ZnO by Cu particles [12]; iv) Cu-Zn alloy [9]. Yurieva and co-workers proposed the dynamic behaviour of Cu particles during reducing/reaction conditions in binary Cu/ZnO system [11]. In their model, Cu atoms migrate from the micro-voids in ZnO matrix towards the ZnO surface during reduction at 520 K, forming platelets. During the reaction in syngas at 520 K these platelets return to the cavities in ZnO lattice (this Cu migration is seen as a reversible process [11]).

Based on LEIS study of Cu/ZnO based catalysts [13], Jansen et al. reported about the formation of ZnO\(_x\) layer on top of Cu particles during the reduction at 500-700 K. This effect of Cu clusters coverage by a thin ZnO layer at the surface contradicts with the Cu platelets theory [11]. Such diversity in opinions reflects the difference in catalyst preparation/treatment parameters, such as copper content, preparation methods, reduction and reaction conditions. Previously, Brands et al. confirmed that both the structure of Cu/ZnO based catalysts and methanol synthesis activity are strongly influenced by the reduction temperature [14]. Similarly, King and Nix reported that the optimal reduction temperature for the binary Cu/ZnO catalyst is 500-600 K, as higher temperatures cause sintering of the copper particles [15]. However, the study by Jansen et al. on silica-supported catalysts showed that the Cu particles are covered by a ZnO layer and thus sintering is prevented [13]. To understand this system better, we study here the interactions between Cu and ZnO using a binary system with the same copper content as in a highly active catalyst [14]. Our
model catalyst is Cu deposited on a ZnO (0001)-Zn surface. In the following sections we describe the catalyst preparation, characterisation, and the structural changes that occur on the surface during a treatment that simulates the operating reduction conditions.

6.2 Experimental

6.2.1 Instrumentation

Measurements were performed in the same setup and similar conditions as described in Chapter 5 [17].

6.2.2 Preparation of the model Cu/ZnO catalyst

Prior to Cu deposition the ZnO (0001)-Zn surface was cleaned by cycles of Ar⁺ ion bombardment (1 keV) at 298 K and subsequent annealing to 1000 K [17]. A typical cleaning cycle consists of Ar⁺ sputtering for 20 min (3.5 × 10⁻⁶ mbar, 1 keV, 10 mA) followed by annealing at 1000 K in UHV for 15 min. ZnO surface was considered as clean when no contaminants were detected by XPS and a triangular reconstruction was observed by STM [17]. Normally after 15-20 cleaning cycles the surface was sufficiently clean for Cu deposition. Note that achieving an atomic-scale resolution is extremely difficult, mostly due to the poor conductivity of ZnO samples. In order to see the changes at the nanometer scale the substrate surface should be prepared as clean and atomically flat as possible.

Copper vapour (99.999% pure) was deposited onto the clean ZnO (0001)-Zn surface at 300 K by Omicron evaporator EV3 [16]. A stable flux current (Cu⁺) of 5.0 nA was used for Cu deposition. Clean ZnO surface was in front of the evaporator nozzle at about 8 cm distance. The total pressure during Cu deposition remained below 5 × 10⁻¹⁰ mbar, which is slightly higher than the base pressure. A deposition rate of 0.083 Å s⁻¹ was used in all the experiments. The deposition rate was calibrated and checked with STM by statistical analysis of the island densities and heights. The height of the clusters was measured from the top of each cluster to the terrace by line profile option. The width was measured on the cluster’s profile cross-section between the points on the base line where the profile line starts to bend upwards. The tip convolution effect due to the finite size of the STM tip was taken into account using the tables [18]. The height of Cu (111) monolayer was calculated to 2.2 Å [16]. All STM images were recorded at a positive sample bias of 3.0 V and with a tunnelling
current of 1.0 nA. Throughout the paper, the concentration of the deposited metal is given in monolayer equivalent (ML), which corresponds to the Cu (111) packing density of $1.7 \times 10^{15}$ Cu atoms per cm$^2$.

### 6.2.3 Annealing of Cu/ZnO (0001)-Zn system in UHV

The annealing was carried out in preparation chamber at a base pressure of $2 \times 10^{-10}$ mbar. The single crystals were heated radiatively, and the temperature was monitored by a thermocouple spot-welded on the heating stage. The temperature difference between heating stage and the sample holder was taken into account [16], and subtracted from the readings of the thermocouple. After cooling down to 373 K, the sample was transported to the analysis chamber for STM measurements. The annealing was kept for 30 min at appropriate temperature. The cooling to 373 K took ca. 15 min. Transferring samples to the analysis chamber took ca. 5 min. Temperature drifts in the STM images were avoided by cooling down the sample in a massive manipulator for 10 min to about 300 K. Thus, the average overall transfer time between annealing and STM measurement was 30 min.

### 6.2.4 Reduction of the model Cu/ZnO (0001)-Zn catalyst

The ZnO single crystal was first cleaned by sputtering and annealing cycles prior to Cu deposition. Then, copper was deposited on this clean ZnO surface. The resulting Cu/ZnO catalysts were annealed in UHV at 700 K for 30 min, and then exposed to $10^{-5}$ mbar H$_2$ in the reaction cell for 30 min at 500 K. After cooling down in the H$_2$ atmosphere to about 370 K, the hydrogenated Cu/ZnO samples were transferred to the UHV chamber for STM and XPS analysis. Similarly, the Cu/ZnO catalysts were reduced at 600, 700, 800, and 900 K.

Note that for each reduction treatment a fresh Cu/ZnO surface was prepared. Every step in this experimental sequence was followed by STM/XPS analysis. The STM/XPS analysis was combined with a thermal desorption spectroscopy (TDS) only for the reduced Cu/ZnO catalysts.
6.2.5 Thermal Desorption Spectroscopy of the hydrogenated Cu/ZnO surface

TDS results on reduced Cu/ZnO system were obtained by the same procedure as described for ZnO single crystal [17]. After STM and XPS analysis of the reduced Cu/ZnO catalysts the samples were transferred to the preparation chamber and heated in UHV from 300 K to 1000 K at 18 K/min. The composition of the desorbing species was monitored with the MS. Contributions from a similarly treated bare sample plate and the heating stage, although small, were subtracted from the TDS curves of the reduced Cu/ZnO catalyst. About 10 min prior to the thermal desorption measurements, the TSP and IGP pumps were switched off to exclude any desorption from hot filaments. The preparation chamber was pumped by the turbo-molecular pump with a speed of 520 l/s, thus minimizing re-adsorption.

6.3 Results and discussion

The model proposed by Yurieva et al. [11] is based on a combined XRD/TEM analysis. It is extremely difficult to monitor the surface modifications of nanoclusters directly during the reduction/reaction processes to clarify the contradiction. Instead, we studied the dynamic behaviour of Cu nanoparticles in Cu/ZnO catalyst system. To do this, we applied a combination of surface probing techniques: Scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), XPS and TDS in monitoring the interaction of Cu and ZnO (0001)-Zn triangular reconstruction in as deposited state and after annealing/reduction treatments. Will this reconstruction remain after Cu deposition? Would the step edges be the preferential nucleation sites for growth of Cu islands? How will copper grow on this surface [20], and how Cu will behave upon annealing in UHV and/or reducing environment? As mentioned previously [17], the choice of the plane was made because of its highest availability in polycrystalline ZnO catalyst. Thus, answering these questions may give us new insights about the formation and structure of the active site of the Cu/ZnO powder catalyst.
6.3.1 Scanning Tunneling: Microscopy and Spectroscopy

6.3.1.1 Growth of Cu on ZnO (0001)-Zn surface

The growth mechanism of Cu on ZnO was studied by several groups. According to Campbell et al. [21], who studied Cu growth on ZnO (0001)-O, Cu grows two dimensionally up to 0.33 ML and then three dimensionally. 2D growth is observed up to a certain critical island size due to kinetic limitations at low temperatures [21, 22]. This shows the importance of the kinetics of metal adatom diffusion along oxide surfaces, since it can prevent the forming of the thermodynamically stable structures. Copper growth on different faces of ZnO has been studied by X-ray photoelectron spectroscopy, low energy ion scattering [22, 23], and electron energy loss spectroscopy [22, 24, 25]. The initial growth stage (i.e. up to several monolayers) is still somewhat controversial. Although there is a general agreement that Cu grows in an island mode, the dimensions of the clusters and the dependence of their morphology on sample orientation and preparation are still debated. An earlier study reported that the first monolayer wets the oxide substrate [24]. More recent studies indicated that the ad-metal grows two-dimensionally only to a certain critical coverage, above which it forms 3D islands [23, 26, 27]. In terms of structural resolution and real-space probing, scanning tunnelling microscopy is the most powerful technique, and a direct visualization study could help to resolve this issue. Unfortunately, STM data are scarce even for clean polar and non-polar ZnO surfaces [28, 29].

Here, we used STM to image Cu on ZnO (0001)-Zn surface. We tailored the amount of copper such that it grows as platelets of about 3 nm diameter, mimicking the sizes of the copper clusters in actual powder catalysts [10, 11]. For this, a tiny copper amount of 0.05 ML was deposited on the ZnO (0001)-Zn surface at 300 K. The coverage was calculated based on the copper amount is deposited. This is in agreement with the amount calculated from XPS spectra. The two dimensional platelets, expected to form at this coverage, have high surface area and therefore high interface area which leads to high number of active sites [1-3, 14, 30, 31].

A freshly prepared clean surface of ZnO (0001)-Zn [17], with the triangular reconstruction on the surface, serves as a substrate for the deposition of Cu clusters. The STM image of deposited Cu clusters is presented on Fig. 1a. These are round platelets of 20-30 Å in diameter and 3-6 Å in height and are homogeneously dispersed on the surface. This indicates that Cu is still in 2D growth regime at such
low coverage. Although the surface contains many energetically favourable sites for nucleation such as steps of the triangular islands and pits, we did not observe any preferential nucleation sites here. Possibly similar dimensions of Cu and Zn atoms favour 2D growth of Cu on ZnO surface [32].

6.3.1.2 Annealing the Cu/ZnO (0001)-Zn system in UHV

An annealing in UHV could strongly influence the nature of the Cu clusters on ZnO surface. Annealing in UHV at different temperatures is in some extent comparable with reducing conditions due to extremely low oxygen content. Therefore the annealing precedes the reduction treatment due to a possible coverage of Cu by ZnO layer even in UHV.

We found that after annealing at 450 K the cluster dispersion and sizes were similar to the ‘as deposited’ state (Fig. 1a). The clusters were started growing after annealing at 475 K (not shown) from ca. 25 Å to 50 Å in diameter. Simultaneously, their height increased from 3-6 Å to 10-20 Å. These clusters were stable up to 600 K.

Fig. 1. STM images (100x100 nm$^2$) of Cu clusters on ZnO (0001)-Zn: as deposited at 300 K (a); annealed in UHV at 600 K (b); 700 K (c); 800 K (d).
Above 600 K, their concentration started decreasing (Fig. 1b), and they completely disappeared from the surface at 700 K. The triangular reconstruction of the ZnO surface also gradually changed until 700 K, with large triangular islands replaced by many small triangular pits and islands (Fig. 1c). At 700 K, the large flat terraces of the initial surface (Fig. 1a) were completely replaced by small steps in the annealed surface (Fig. 1c). This remained stable after annealing at 800 K (Fig. 1d).

We hypothesised that the copper clusters disappeared from the surface after annealing at 700 K either by sintering or the formation of a ZnO layer over copper. The first hypothesis was excluded after numerous scans at various locations and different magnifications. No copper clusters were found on the surface after annealing at 700 K. We therefore maintain the second hypothesis of buried copper clusters.

The Cu coverage by ZnO species after annealing at 700 K is similar to the behaviour of the Cu/ZnO in H₂ reported previously [10]. Indeed the UHV conditions are comparable to the reducing conditions in view of extremely low oxygen content [17]. Moreover, this indicates that the thermal energy at 700 K suffices for Zn species to migrate over the Cu clusters. As Table 1 shows, this significantly lowers the surface free energy.

The oxygen atoms decorate the steps of dominant triangular features, pits and islands, this was observed previously [35]. More small triangles result in higher concentration of available Zn. The mobility of Zn atoms is higher than that of ZnO species, thus it is likely that Zn atoms cover the Cu clusters first. This coverage does not exclude alloying at such high temperatures, and brass formation will also lower the surface free energy (Fig. 2c, Table 1).

<table>
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<tr>
<th>Table 1. Surface free energy (γ) of metals [33] and oxides [34]</th>
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<tr>
<td>γ (mJ/m²)</td>
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<td>Zn (0001)</td>
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Fig. 2. STM images (200×200 nm²) of Cu/ZnO (0001)-Zn: as deposited at 300 K (a) and subsequent annealing in UHV at 700 K prior to H₂ exposure (b). Scheme of the Cu/ZnO transformation towards Cu clusters coated by Zn-Cu alloy (c): 1) Cu cluster deposited on clean ZnO (0001)-Zn face (a); 2) annealing process at 700 K - the Cu clusters are covered by ZnO layer (b); 3) reduction treatment at 700 K - metallization of the surface via Zn surface enrichment and Zn-Cu surface alloy formation.

Note that such modification of triangular reconstruction at 700 K requires copper (Fig. 1c) (the initial clean ZnO surface was prepared by annealing at 1000 K, with relatively large terraces (Fig. 1a)). Ostendorf et al. [36] reported about facets in the form of highly regular step arrays when ZnO is annealed above 1150 K. Our findings mean that Cu promotes ZnO reduction by means of small triangular features and/or stabilises this reconstruction during cooling to 300 K. The formation of these small triangles could result in lower adsorption barriers and/or higher sticking probabilities of adsorbed gas molecules on step edges, which is important for reaction pathway.

6.3.1.3 Reduction in H₂

As explained above, annealing of the freshly prepared Cu/ZnO surface (Fig. 2a) in UHV for 30 min at 700 K, caused the Cu clusters disappearance from the ZnO surface (Fig. 2b). To monitor the
dynamic behaviour [11] by STM the annealed surface was exposed to $10^{-5}$ mbar H$_2$ at different temperatures for 30 min and analysed it with STM (Fig. 3).

The clusters do not reappear after reduction treatment at 500 K in the same amount as it might be expected according to Yurieva’s model [11] (see Fig. 3a). The triangular reconstruction is still visible, in contrast with the pure ZnO surface reduced at 500 K [17]. In fact, the small triangles dominate on the surface reduced at 500 K.

After reduction treatments at 600-800 K the surface gets even rougher, and observing the copper clusters becomes difficult. The roughness is higher than the cluster height, and the clusters might also be covered by a ZnO layer. The images of Cu/ZnO reduced at 600-700 K show many bright round features about 10-20 nm in diameter (Fig. 3b-c). These are likely islands of metallic Zn and/or hydrogen ad-layers, because the amount of metal, which can be estimated from the number and sizes of these spots, exceeds by far the 0.05 ML of deposited copper. The image of the surface reduced at 800 K (Fig. 3d) contains smaller number of round grains with about 3-5 nm size. It also shows a clear terrace growth direction. These terraces are quite narrow, ~5 nm in width.

Fig. 3. STM images (200 x 200 nm$^2$) of Cu/ZnO (0001)-Zn: after exposure to $10^{-5}$ mbar H$_2$ for 30 min at different temperatures: 500 K (a); 600 K (b); 700 K (c); 800 K (d).
The STS measurements show that hydrogen treatment partially reduces the ZnO surface to metallic zinc (Fig. 4). Note that the shift in the I-V curve to a metallic character is most pronounced for the hydrogen treated surface. In summary, the STM results on Cu/ZnO system differ from that of pure ZnO, especially for 500 and 800 K [17]. It is unclear how these differences are influenced by a small amount of copper. Nevertheless, our STS results (Fig. 4) show a bigger shift towards metallic character in the I-V curves of copper-containing ZnO surfaces. This means that the reduction of the Cu/ZnO system is stronger compared to pure ZnO. This enhanced reduction is caused by an interaction with copper.

Fig. 4. I-V curves for the Cu/ZnO (0001)-Zn surface shown in Figs. 2a-b, and the surfaces exposed to 10⁻⁵ mbar H₂ at 700 K shown in Fig. 3c.

6.3.2 X-ray Photoelectron Spectroscopy

Following the STM and STS studies, we used XPS for probing the modifications on the Cu/ZnO surface after exposure to hydrogen. The results confirm that the degree of surface modification strongly depends on reduction temperature. Here the most informative XPS lines were Cu 2p₃/₂ (Fig. 5) and O 1s (Fig. 6). The peak of the Zn 2p₃/₂ line remained stable within the treatments. A very weak signal of C 1s peak was present only in hydrogen treated samples, meaning that either the hydrogen gas was contaminated or the heated surroundings were slightly polluting the reaction chamber. The binding energy of Cu 2p₃/₂ peak of initial Cu/ZnO surface is 932.6 eV, indicating metallic copper. Moreover, annealing at 700 K in UHV caused only a
small decrease in the intensity of Cu peak. This confirms the presence of Cu on the annealed surface. The intensity decrease correlates with coverage of Cu clusters by a thin Zn layer.

After exposing this catalyst to hydrogen at 500 K, the Cu 2p\textsubscript{3/2} peak broadened slightly and the intensity was decreased (Fig. 5), probably reflecting an alloying between Cu and Zn (broadening due to the partial oxidation of Cu can be excluded in view of reducing conditions and lower oxidisability of Cu as compared to Zn).

The decrease of the Cu 2p\textsubscript{3/2} peak intensity (Fig. 5) may reflect the increased surface roughness (see Fig. 3) caused by zinc hydroxide. The hydroxide formation is confirmed by the increased contribution of hydroxyl group at the higher binding energy side of O1s peak (Fig. 6). Note that the intensity of Cu 2p\textsubscript{3/2} peak has gradually decreased further at higher reduction temperatures. This may reflect an increased Cu coverage by ZnO\textsubscript{x} species that is explained by the limited escape depth of collision-free photoelectrons from buried Cu clusters. The clear chemical shift of the Cu 2p\textsubscript{3/2} to higher binding energy of 933.1 eV after reduction at 800 K (Fig. 5) is attributed to the increased Cu/Zn alloy contribution (a similar reasoning applies to the surface reduced at 900 K). Unfortunately, we could not extract more detailed information from X-ray induced Auger lines of Zn LMM.

**Fig. 5.** XPS showing the Cu 2p\textsubscript{3/2} spectra of copper deposited on ZnO (0001)-Zn surface, Cu/ZnO surface annealed at 700 K in UHV and after exposure to 10\textsuperscript{-5} mbar H\textsubscript{2} for 30 min at 500-900 K.
6.3.3 Thermal Desorption Spectroscopy

Examining the TDS results (Fig. 7), shows that the hydrogen desorption profile for Cu/ZnO is similar to that for ZnO. There are two main peaks resolved in both systems, regardless of the reduction temperature. However, there are also differences: Cu/ZnO catalyst reduced at 300 K desorbs more H\textsubscript{2} at 980 K compared to ZnO exposed to H\textsubscript{2} at 300 K [17]. This difference in H\textsubscript{2} uptake is a result of the enhanced H\textsubscript{2} absorption at 300 K. The increased H\textsubscript{2} absorption by the annealed Cu/ZnO system could be caused by an effective H\textsubscript{2} splitting on increased amount of step edges of annealed at 700 K Cu/ZnO surface or Cu-Zn alloy sites and the subsequent diffusion of atomic hydrogen into the ZnO lattice [37]. As this hydrogen is trapped in the copper-modified ZnO subsurface [38], it desorbs at relatively high temperatures. Similarly, Cu/ZnO reduced at 500 K has higher H\textsubscript{2} desorption yield (Fig. 7) than ZnO at desorption temperatures >830 K.

As we previously showed [17], reduction at 500 K will not reduce ZnO to Zn and split hydrogen, while in Cu/ZnO hydrogen splitting may take place on increased amount of ZnO step edges or Cu sites. Interestingly, that the pure ZnO has higher H\textsubscript{2} uptake than Cu/ZnO at elevated temperatures (Fig. 7). Cu/ZnO reduced at 800 K has H\textsubscript{2} desorption about one order of magnitude lower than ZnO.
Fig. 7. \( H_2 \) desorption from the ZnO [17] and Cu/ZnO surfaces being reduced at 300-800 K upon annealing in UHV. The vertical lines at the end represent the hold-period after the final temperature was reached. Please note the logarithmic vertical scale.

Fig. 8. Zn desorption from the ZnO data from Ref. [17] and Cu/ZnO surfaces being reduced at 300-800 K upon annealing in UHV.
reduced at 800 K. This indicates the formation of the metallic zinc on ZnO surface which effectively splits hydrogen molecules. The smaller amount of H$_2$ desorbed from Cu/ZnO reduced at 800 K can be related to the Cu coverage by ZnO$_x$ species and Cu-Zn alloy formation [10, 30], perhaps the alloy sites are less efficient in H$_2$ splitting as pure Zn. Except for the dissociation sites, absorption of hydrogen increases at higher temperatures because of increased hydrogen diffusion.

Although Zn desorption behaviour from Cu/ZnO system has similar profile as pure ZnO (Fig. 8), there are some remarkable differences. Desorbed Zn is at least an order of magnitude higher for pure ZnO. Moreover, Zn desorption starts at 460 K for pure ZnO and at 530 K for Cu/ZnO. This indicates that Cu stabilizes Zn from evaporation which was also observed previously [10]. This stabilisation is probably caused by Cu-Zn alloying.

6.4 Conclusions

The reduction of the ZnO surface in our model methanol synthesis catalysts occurs by means of increased amount of small triangular features decorated with oxygen atoms. Copper plays a promoting role in this reduction. The alloying between copper and zinc stabilises both early Zn evaporation and H$_2$ desorption below 500 K. Our findings agree with the previous LEIS work [13]. We conclude that the activated catalyst surface consists of Zn-Cu alloy sites. Moreover, our results show that a higher interstitial H$_i$ concentration is available for the reaction at the methanol synthesis temperature of 520-550 K. Importantly, these effects can strongly influence catalytic methanol synthesis, as the ZnO surface could act as a hydrogen “supply point” for the reaction.

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