

Dynamical changes in Cu/ZnO/Al₂O₃ catalysts

H. Wilmer and O. Hinrichsen *

Ruhr-University Bochum, Laboratory of Industrial Chemistry, D-44780 Bochum, Germany

Received 14 March, 2002; accepted 29 April 2002

A combination of various transient and steady-state kinetic experiments was used to provide evidence for dynamical changes in a Cu/ZnO/Al₂O₃ catalyst of industrial interest. From these it can be deduced that the reversible structural alterations strongly depend on the reaction conditions as well as on the pretreatment. The pretreatment was found to induce changes in the morphology of the metallic Cu particles to some extent, and surface alloying under more severe reducing conditions.

KEY WORDS: Cu/ZnO/Al₂O₃ catalyst; methanol synthesis; dynamic behavior; temperature-programmed desorption of H₂; N₂O reactive frontal chromatography.

1. Introduction

The copper/zinc oxide catalyst containing alumina is industrially important for methanol synthesis from gas mixtures consisting of H₂, CO₂ and CO [1]. It was reported that morphological changes of the Cu particles significantly influence the catalytic activity in methanol synthesis [2–6]. The development of *in situ* methods such as EXAFS and XRD allowed the extraction of quantitative short- and long-range structural information on a heterogeneous catalyst [7–9]. The Topsøe group has been particularly active in this area, applying these techniques and catalytic studies to obtain *in situ* data on structural changes [4–6] and to follow dynamical changes occurring under reaction conditions [3,5]. Their results for a 5% Cu/ZnO catalyst revealed that the Cu–Cu coordination number for Cu metal particles on ZnO changed reversibly depending on the gaseous atmosphere applied. These observations led to a dynamic model that correlated the relative interfacial area between Cu metal and ZnO in Cu–ZnO with the reduction of the ZnO component and the consequent spreading of Cu metal species on ZnO [4]. Finally, the Topsøe group integrated the dynamical changes into a microkinetic model which can be used for extrapolation to industrial relevant reaction conditions [10].

Recently, Topsøe and Topsøe [11] applied infrared spectroscopy of CO adsorption in order to study the formation of Cu–Zn surface alloys (1 and 5% Cu on ZnO) under more severe reduction conditions. It was found that the formation and destruction of the surface alloy occurs reversibly. New results confirm the dynamic changes of the Cu particles as well as the surface alloying under severe reducing reaction conditions [6]. Investigations on Cu/ZnO catalysts with various reducing agents

by Jung *et al.* [12] proved that ZnO can be reduced with CO or methanol in the presence of Cu giving rise to brass formation under highly reducing conditions in good agreement with ref. [13].

In our study, a combination of the temperature-programmed desorption of H₂ (H₂ TPD) [14,15], N₂O reactive frontal chromatography (N₂O RFC) [16] and flow-switching experiments was applied to characterize the state of a coprecipitated ternary catalyst (50% Cu, 35% ZnO and 15% Al₂O₃). The choice of the pretreatment gas and the duration of pretreatment were found to have a significant impact on the methanol synthesis activity. In particular, H₂ TPD followed by N₂O RFC was used in order to prove the state of the working catalyst under reaction conditions close to industrial operation.

2. Experimental

The experiments were carried out in a flow set-up equivalent to that described in refs. [14,15]. The following gases of high purity were used: He (99.9999%), H₂ (99.9999%), CO/He (10% CO, 99.9995%), CO₂/He (4% CO₂, 99.9995%), N₂O/He (1% N₂O, 99.9995%), H₂/He (2.1% H₂, 99.9995%) and a mixture of 72% H₂, 10% CO and 4% CO₂ in He used as methanol synthesis feed gas (99.9995%), termed synthesis gas in the following. The synthesis gas was further purified by means of a guard reactor filled with ZnO to adsorb impurities such as sulfur and chlorine compounds. Fast on-line gas analysis was performed by a calibrated quadrupole mass spectrometer (Balzers GAM 422).

The kinetic experiments were carried out with a ternary Cu/ZnO/Al₂O₃ catalyst with approximate overall composition of 50% CuO, 35% ZnO, and 15% Al₂O₃ prepared by sodium carbonate precipitation of

* To whom correspondence should be addressed.
E-mail: olaf@techem.ruhr-uni-bochum.de

mixed nitrate solutions of the metals followed by filtration, washing, drying and calcination [1]. In this study, 200 mg of the 250–355 µm sieve fraction were filled into the reactor consisting of a glass lined U-tube with an inner diameter of 4 mm resulting in a bed height of about 20 mm. The reduction of the catalyst was carried out with the H₂/He mixture ramping the temperature at 1 K min⁻¹ to 513 K. The catalytic activity under steady-state conditions was determined at 473 K and at atmospheric pressure using synthesis gas at a flow rate of $Q = 75 \text{ N ml min}^{-1}$.

The temperature-programmed desorption of H₂ (H₂ TPD) was carried out as follows: pretreatment of the catalyst was done at 493 K by flowing either CO/He or synthesis gas over the catalyst followed by flushing in He at 493 K for 0.5 h. The reactor was rapidly cooled down to 240 K, which was found to be the optimum dosing temperature [15]. Complete saturation with adsorbed atomic hydrogen was achieved by dosing pure H₂ for 0.5 h at 1.5 MPa. Subsequently, the pressure was reduced to atmospheric pressure and the oven was rapidly cooled down to 78 K. Finally, the gas flow was changed to He in order to flush the catalyst for a further 30 min. Then the H₂ TPD experiment was carried out by ramping the temperature linearly at 6 K min⁻¹ to 493 K ($Q_{\text{He}} = 100 \text{ N ml min}^{-1}$). Additionally, N₂O reactive frontal chromatography (N₂O RFC) was used to measure the specific metallic Cu surface area according to the method proposed by Chinchen *et al.* [16] at somewhat more moderate reaction conditions [17]. Then, the catalyst was heated to 473 K (6 K min⁻¹) in synthesis gas in order to measure the catalytic activity at steady state.

3. Results

The temperature-programmed desorption technique of H₂ [14,15] was applied for the characterization of the state of the working catalyst by varying the duration of CO/He pretreatment. The subsequently obtained H₂ TPD spectra are displayed in figure 1. Spectrum A was recorded after

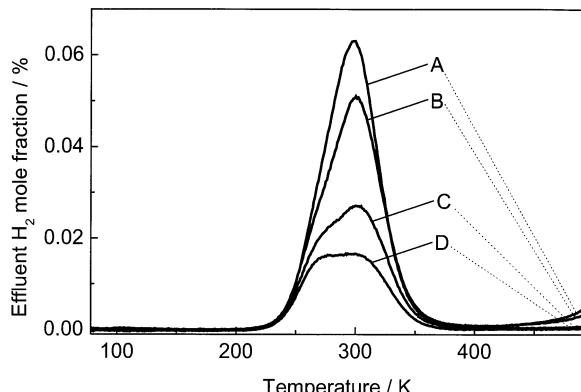


Figure 1. H₂ TPD spectra after pretreatment of the Cu/ZnO/Al₂O₃ catalyst with CO/He for (A) 0 h, (B) 1 h, (C) 18 h and (D) 64 h. Experimental conditions: $\beta = 6 \text{ K min}^{-1}$, $Q_{\text{He}} = 100 \text{ N ml min}^{-1}$, $w_{\text{cat}} = 0.2 \text{ g}$.

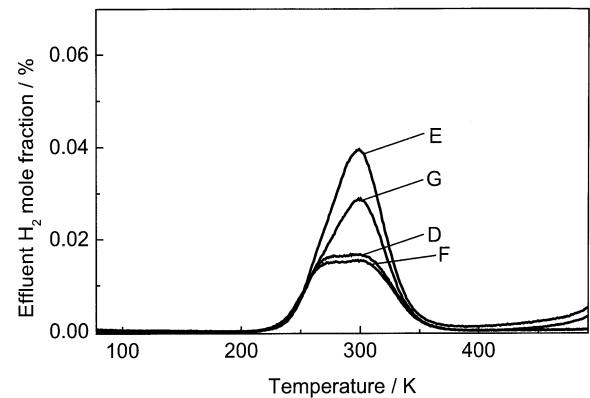


Figure 2. H₂ TPD spectra after pretreatment of the Cu/ZnO/Al₂O₃ catalyst with (D) CO/He in He for 64 h, (E) synthesis gas for 19 h, (F) CO/He for 62 h and (G) synthesis gas for 0.5 h. Experimental conditions: $\beta = 6 \text{ K min}^{-1}$, $Q_{\text{He}} = 100 \text{ N ml min}^{-1}$, $w_{\text{cat}} = 0.2 \text{ g}$.

reduction followed by carrying out methanol synthesis for 12 h. A symmetrical TPD signal was observed with a peak maximum at 296 K similar to that published in ref. [15]. In a first series of TPD experiments, the catalyst was treated with CO/He at 493 K for 1, 18 and 64 h. After 1 h pretreatment with CO/He (trace B) the amount of desorbed H₂ decreased by 13%. Additionally, a slight asymmetry appeared. The formation of the low-temperature shoulder became evident after 18 h CO/He pretreatment (trace C). A further significant decrease in the amount of desorbed H₂ was observed. Finally, a prolongation of the CO/He pretreatment up to 64 h (trace D) led to a TPD profile with two pronounced maxima located at about 275 and 300 K. Furthermore, an increase of the baseline starting at a temperature of 450 K for traces A and B was detected.

In order to check the reversibility of the previously described phenomena, additional TPD experiments with alternating pretreatment cycles were performed (figure 2). Spectrum D is identical with trace D in figure 1, i.e. conducted after 64 h CO/He. Treating the catalyst subsequently with synthesis gas for 19 h resulted in an increase of the amount of H₂ in the TPD spectrum. The shape of the TPD profile resembles trace B in figure 1. Changing repeatedly to the more severe CO/He pretreatment of 62 h led to spectrum F, which is almost identical to D. A slight decrease in the amount of desorbed H₂ was observed. Finally, running methanol synthesis for 0.5 h prior to the TPD resulted in trace G, which is located between E and F.

We used the instantaneous adsorptive decomposition of N₂O (N₂O + 2 Cu → N₂ + Cu₂O) in an isothermal flow experiment as a fast and reliable method for the determination of the specific Cu metal surface area in a standardized procedure [16] under moderate reaction conditions [17]. Subsequent to each H₂ TPD experiment, N₂O RFC was performed in order to compare the results obtained by both methods. In figure 3, methanol activity recorded under steady-state reaction conditions is

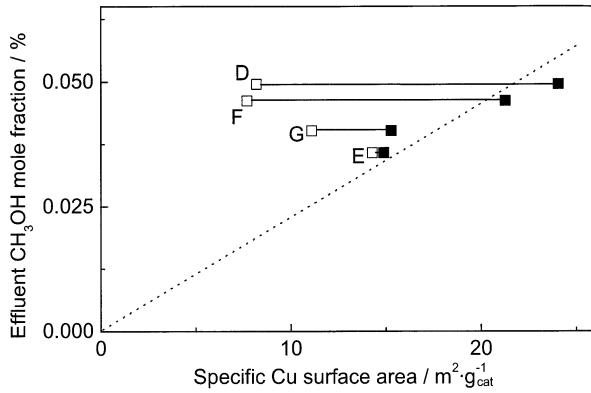


Figure 3. N₂O frontal chromatography (filled squares) and H₂ TPD method (open squares). Pretreatment procedure: (D) CO/He for 64 h, (E) synthesis gas for 19 h, (F) CO/He for 62 h and (G) synthesis gas for 0.5 h. Experimental conditions: $T = 473\text{ K}$, $p = 0.1\text{ MPa}$, $Q = 75\text{ N ml min}^{-1}$, $w_{\text{cat}} = 0.2\text{ g}$.

plotted against the specific Cu surface area determined by N₂O RFC (filled squares). The graph demonstrates a linear correlation between methanol production and specific Cu surface area as indicated by the linear regression line. Corresponding results from the H₂ TPD method prior to N₂O RFC (open squares) are connected by horizontal lines. After a long pretreatment with synthesis gas (experiment E) the two methods yielded similar specific Cu areas of about $15\text{ m}^2\text{ g}_{\text{cat}}^{-1}$ based on a mean atom density of $1.47 \times 10^{19}\text{ Cu atoms per m}^2$. Experiments D and F were conducted after CO/He pretreatment for 64 h and 62 h, respectively, leading to a high N₂O consumption. The slight decrease in surface area determined from trace F compared to D was caused by sintering of the catalyst during the test series. Accordingly, the specific Cu surface area is higher compared with the value determined by the H₂ TPD method. Experiment G was conducted subsequent to F, followed by carrying out methanol synthesis for 0.5 h. Despite the short duration of the pretreatment, the decrease of difference in the surface area is enormous, which clearly emphasizes the significant impact of both pretreatments on the catalytic activity.

The dynamic behavior of the Cu/ZnO/Al₂O₃ system was confirmed by a switching experiment from pretreatment gas to synthesis gas at constant reaction temperature in the following way: the catalyst was treated for 0.5 h with different pretreatment gases (CO/He (A), He (B), H₂ (C) and CO₂/He (D)) at 473 K and atmospheric pressure. Subsequently, the initial methanol production was measured for 0.5 h at atmospheric pressure. The results for four measurements are displayed in figure 4. Traces A and B were obtained within the first series of experiments while C and D were recorded with a new loading of the same catalyst. Hence, the activity is expressed as a normalized production rate and scaled to the maximum normalized production rate obtained at steady state in each series of experiments. Additional

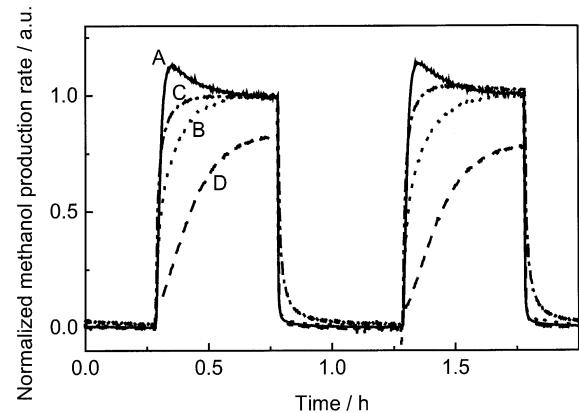


Figure 4. Normalized methanol production rate after pretreatment of the Cu/ZnO/Al₂O₃ catalyst for 0.5 h with (A) CO/He, (B) He, (C) pure H₂ and (D) CO₂/He subsequent to switching to synthesis gas (72% H₂, 10% CO, 4% CO₂, 14% He). Experimental conditions: $T = 473\text{ K}$, $p = 0.1\text{ MPa}$, $Q = 75\text{ N ml min}^{-1}$, $w_{\text{cat}} = 0.2\text{ g}$.

tests proved that almost no deactivation of the catalyst was found upon carrying out both pretreatment/activity cycles in the total run of the presented experiments. Repetition of the pretreatment/activity cycles displayed in figure 4 revealed the good reproducibility of the experimental findings. The deviations in the initial methanol activity caused by the use of different gases are, however, significant.

After the pretreatment either with He (trace B) or H₂ (trace C) the steady-state activity was reached relatively quickly, while the pretreatment with the highly reducing CO (trace A) led to a sudden increase of the methanol activity followed by an overshoot. After a few minutes the activity leveled off. In the case of the CO₂ pretreatment (trace D), the methanol production rate increased very slowly and did not achieve steady state during the measurement. A closer inspection of the kinetic data for the CO₂ pretreatment reveals that the methanol activity slightly decreased in the repeated experiment. Additional switching experiments (not shown here) confirmed a further decrease in catalytic activity.

In the case of methanol synthesis, the data acquisition strongly depends on the state of the catalyst. In a previous paper by Bielawa *et al.* [18], it was illustrated that the temperature-programmed way of collecting kinetic data in methanol synthesis was limited due to a slow change of the state of the working Cu/ZnO/Al₂O₃ catalyst. A long-term experiment was conducted in the following way: the specific Cu surface area was determined by N₂O RFC at 300 K subsequent to the H₂ TPD experiment (trace D) in figure 2 (CO/He pretreatment at 493 K for 64 h). Then, the catalyst was heated to 473 K (6 K min^{-1}) in order to measure the catalytic activity under steady-state conditions. Figure 5 displays the change in methanol activity at the beginning of the measurement and after 20 h. Compared with the dosing conditions applied for trace A in figure 4 (CO/He pretreatment at 493 K for 0.5 h), a longer pretreatment

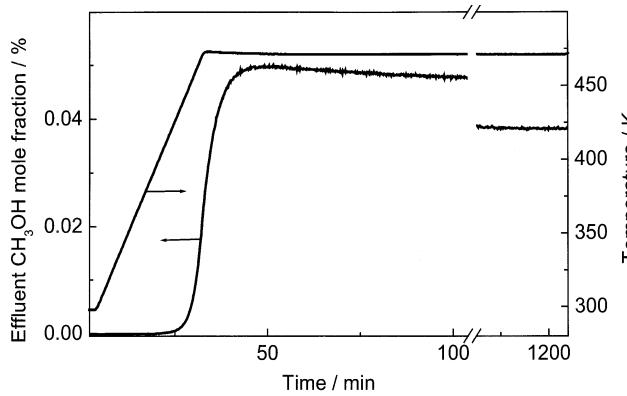


Figure 5. Methanol activity of the Cu/ZnO/Al₂O₃ catalyst. Pretreatment procedure consisted of flowing CO/He for 64 h at 493 K. Experimental conditions: $T = 473\text{ K}$, $p = 0.1\text{ MPa}$, $Q = 75\text{ N ml min}^{-1}$, $w_{\text{cat}} = 0.2\text{ g}$.

of the catalyst with CO/He obviously led to a more pronounced maximum in methanol formation. The catalyst showed first no activity, presumably due to blocking of active sites by atomic oxygen. Methanol formation started after 10 min and maximum activity was achieved. It took several hours to achieve steady state. Due to this fact accumulation effects on the catalyst can be excluded.

Further systematic series of pretreatment/activity cycles demonstrated the influence of the different pretreatment procedures on the catalytic activity. Experimental results are shown in figure 6, where the duration of the pretreatment was altered and different sequences of the dosing gases were applied. The maximum initial rate of catalytic activity was achieved by the pretreatment with CO/He for 0.5 h (trace A). The lowest increase was obtained by flushing in pure He (trace G). The curves in between resulted from a combined pretreatment with both dosing gases. In the case of experiment A the catalyst

was treated only with CO/He, in contrast to the subsequent He pretreatment (trace B). The further use of He resulted in a lower initial activity. From the comparison of traces B and C it can be seen that the pretreatment gas used at first had a higher influence on the initial methanol activity. Furthermore, the duration of the pretreatment had an important effect on the initial catalytic activity. Longer pretreatment with CO resulted in a more active catalyst, indicated by the comparison of traces C and E. Accordingly, longer He pretreatment led to an initially less active catalyst (trace D compared to F).

4. Discussion

The results of the presented H₂ TPD experiments demonstrated that changing the pretreatment gas from synthesis gas to CO/He significantly altered the shape of the TPD profile. Accordingly, a strong decrease was observed in the height of the TPD signal which revealed two overlapping maxima after longer dosing of CO/He. In general, the temperature of the onset (210 K) and of the end (390 K) of the signal remained constant. In the case of the same pretreatment gas and comparable duration of dosing (e.g., traces D and F in figure 2) similar signals were obtained. The TPD spectra recovered upon switching back to synthesis gas. A strong metal-support interaction (SMSI) seems to be responsible for the reversible changes. This phenomenon was described by Tauster *et al.* [19] for a similar system, namely metal/TiO₂. The formation of different structures was found to depend strongly on the reduction temperature applied. A low-temperature reduction (473 K) led to highly dispersed particles, whereas high-temperature reduction (773 K) lowers the metallic surface area provided for H₂ or CO chemisorption. It was suggested that TiO_x ($x \leq 2$) species migrate onto the support. Compared with that study, surface alloying between Cu and ZnO_x is therefore expected to occur under the highly reducing conditions applied in our present TPD study.

Large differences in the H₂ uptake (e.g., trace B in figure 1 compared with E in figure 2) can be attributed mainly to sintering of the metallic Cu particles since no significant shift of the peak maximum in the TPD spectra was observed. Sintering accompanied with a loss in catalytic activity is known to occur when severe reaction conditions are applied [20]. Initial deactivation was faster, as indicated by the differences in several experiments (difference in the traces B and E compared with D and F in figures 1 and 2, which were conducted after a longer time on stream). In detailed microkinetic studies, which were done independently in different research groups [15,21], it was suggested that the Cu particles of Cu/ZnO/Al₂O₃ catalysts investigated after pretreatment in synthesis gas mainly exposed Cu(111). When using the pretreatment with CO/He, the TPD

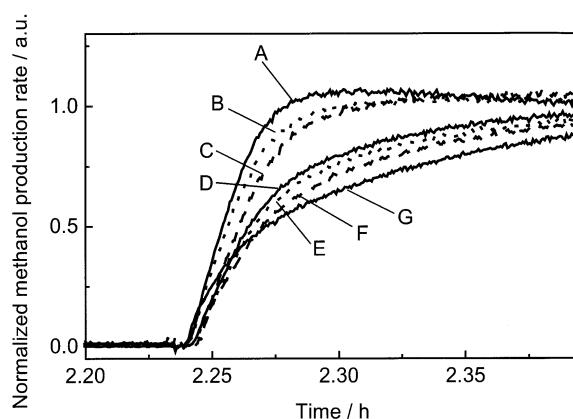


Figure 6. Normalized methanol production rate after pretreatment of the Cu/ZnO/Al₂O₃ catalyst: (A) CO/He for 0.5 h, (B) CO/He for 0.5 h followed by He for 0.5 h, (C) He for 0.5 h followed by CO/He for 0.5 h, (D) He for 0.25, CO/He for 0.5 h followed by He for 0.25 h, (E) He for 0.5 h followed by CO/He for 0.5 h, (F) He for 0.5 h, CO/He for 0.5 h and He for 0.5 h as well as (G) He for 0.5 h. Experimental conditions: $T = 473\text{ K}$, $p = 0.1\text{ MPa}$, $Q = 75\text{ N ml min}^{-1}$, $w_{\text{cat}} = 0.2\text{ g}$.

spectrum is rather dominated by the desorption from other crystal surfaces. In a recent reduction/oxidation study by Sakakini *et al.* [22] the existence of Cu(110) and Cu(211) faces was proposed. In summary, our experimental observations lead to the indirect conjecture that the alternating pretreatment induces reversible structural changes of the catalyst, since the total number of metallic Cu surface atoms derived from the TPD experiments was lowered and the ratio of different surface sites was significantly changed under severe reducing conditions.

The TPD spectra obtained subsequent to running methanol synthesis (traces A and B in figure 1) showed a slight increase in the baseline towards the end of the experiment, giving rise to a minor desorption signal starting at a temperature of 450 K. As discussed in refs. [15,23], the presence of this signal can be attributed to the additional desorption of H₂ which originates from dissociation of water stored on the support. This desorption signal was only observed after synthesis gas pretreatment in contrast to the TPD experiment subsequent to the intensive treatment with CO/He.

The dynamic behavior of the Cu/ZnO/Al₂O₃ catalyst was further investigated by flow-switching experiments with different gases. Steady-state activity measurements with synthesis gas after pretreatment with CO/He as a highly reducing agent revealed that the activity of the catalyst passed through a maximum after a few minutes. Longer pretreatment with CO/He led to a more active state of the catalyst, whereby a quasi-stable state was only achieved after several hours. Subsequent to the pretreatment with H₂ or He no transient maximum of methanol synthesis activity was observed. The pretreatment with CO₂, however, led to a less active state of the catalyst. This phenomenon can be attributed to the oxidation of the catalyst [23]. In summary, the higher the reduction potential of the gas applied for pretreatment (CO > H₂ > He > CO₂), the higher the initial catalytic activity due to structural changes of the catalyst.

Reversible changes of the metallic Cu particles in a Cu/ZnO (5% Cu on ZnO) system were observed in *in situ* EXAFS experiments by Clausen and co-workers [4,6]. By changing the oxidation potential in the synthesis gas mixture it was found that the apparent Cu–Cu coordination number changes, suggesting that the small metallic Cu particles dynamically alter the morphology (wetting/non-wetting behavior caused by spreading of the Cu particles on the support). The modification of the catalyst was a long persisting process, which was shown by different durations of the pretreatment (cf. figure 5). Desorption of stored methanol by replacement with other gases was ruled out in a long-term experiment. The regeneration of the catalyst after flushing with CO lasted several hours. Our findings agree well with experimental results performed with Cu-based catalysts by Muhler *et al.* [3] as well as by

Meitzner and Iglesia [24], who observed a transient behavior of the catalyst upon switching between two different mixtures of synthesis gas.

Subsequent to the CO/He pretreatment the measured amount of H₂ in the TPD spectrum decreased significantly (e.g., trace D in figure 1), which suggests a loss in the specific metallic Cu surface area. This result appears to be diametrical to the increased activity observed after this pretreatment, since it is generally accepted that the specific Cu surface area correlates linearly with the methanol activity [25]. The TPD experiment subsequent to the pretreatment with synthesis gas showed a reversible increase in the uptake of H₂ and, in turn, the assumed correlation between specific Cu surface area (determined according to the H₂ TPD method) and catalytic activity was restored. N₂O RFC was used as an additional method for the determination of the specific Cu surface area. A CO/He pretreatment led here to a higher N₂O consumption, which suggests an enlargement of the Cu surface. Longer dosing of CO/He obviously led to morphology changes, which inhibited the adsorption of hydrogen in the subsequent H₂ TPD. The spreading of Cu in a reducing atmosphere, as reported in the literature [4], cannot explain solely this observation, since this would lead to a higher specific Cu surface area and thus to a higher amount of H₂ determined by the H₂ TPD method. Jung *et al.* [12] provided evidence that the catalyst could be reduced with CO, presumably leading to oxygen vacancies at the Cu/ZnO interface as well as to reversible surface alloy formation. Therefore, our experimental results can be explained in agreement with the dynamic alloying model recently proposed by the Topsøe group [6] as follows: ZnO can be reduced in the presence of Cu by CO creating mobile ZnO_x species on Cu (strong metal support interaction), which inhibit further adsorption of H₂. This entails a smaller amount of H₂ obtained by the H₂ TPD method. In the subsequent N₂O RFC experiment, surface Cu is oxidized to Cu₂O as well as ZnO_x to ZnO. Therefore, after reducing conditions more than only the metallic Cu surface of the Cu/ZnO/Al₂O₃ catalyst is determined by N₂O RFC. Thus, the N₂O RFC is an efficient tool to characterize Cu/ZnO catalysts, since it probes the highly active SMSI state.

5. Conclusions

The H₂ TPD, N₂O RFC and flow-switching experiments were found to be valuable tools to characterize the state of a Cu/ZnO/Al₂O₃ catalyst. A longer pretreatment with CO reduced the height of the H₂ TPD peak significantly, which, in turn, suggests a decrease in the specific metallic Cu surface area. Furthermore, after severe dosing a second maximum in the TPD profile was identified, presumably due to the desorption from different Cu facets.

Alternating pretreatment of the catalyst with CO and synthesis gas demonstrated the reversibility of the structural changes, presumably by a change of the morphology of the metallic Cu particles and by surface alloying between Cu and ZnO_x when severe reducing conditions were applied. In contrast, prolonged pretreatment with CO increased the amount of N₂O consumed during the RFC, indicating that N₂O oxidizes both the Cu surface layer and ZnO_x species.

Steady-state kinetic measurements revealed that the catalytic activity strongly depends on the pretreatment gas applied: the higher the reduction potential, the more active the catalyst, indicating the highly active SMSI state of the Cu/ZnO/Al₂O₃ catalyst.

Acknowledgment

Fruitful discussions with Martin Muhler are gratefully acknowledged.

References

- [1] J.B. Hansen, in: *Handbook of Heterogeneous Catalysis*, Vol. 3, eds. G. Ertl, H. Knözinger and J. Weitkamp (VCH Verlagsgesellschaft, Weinheim, 1997) p. 1856.
- [2] K. Tohji, Y. Udagawa, T. Mizushima and A. Ueno, *J. Phys. Chem.* 89 (1985) 5671.
- [3] M. Muhler, E. Törnqvist, L.P. Nielsen, B.S. Clausen and H. Topsøe, *Catal. Lett.* 25 (1994) 1.
- [4] B.S. Clausen, J. Schiøtz, L. Grabaek, C.V. Ovesen, K.W. Jacobson, J.K. Nørskov and H. Topsøe, *Top. Catal.* 1 (1994) 367.
- [5] H. Topsøe, C.V. Ovesen, B.S. Clausen, N.-Y. Topsøe, P.E. Højlund Nielsen, E. Törnqvist and J.K. Nørskov, *Stud. Surf. Sci. Catal.*, 109 (1997) 121.
- [6] J.-D. Grunwaldt, A.M. Molenbroek, N.-Y. Topsøe, H. Topsøe and B.S. Clausen, *J. Catal.* 194 (2000) 452.
- [7] J.W. Couves, J.M. Thomas, D. Waller, R.H. Jones, A.J. Dent, G.E. Derbyshire and G.N. Greaves, *Nature* 354 (1991) 465.
- [8] A.J. Dent, M.P. Wells, R.C. Farrow, C.A. Ramsdale, G.E. Derbyshire, G.N. Greaves, J.W. Couves and J.M. Thomas, *Rev. Sci. Instrum.* 63 (1992) 903.
- [9] G. Sankar, J.M. Thomas, D. Waller, J.W. Couves, C.R.A. Catlow and G.N. Greaves, *J. Phys. Chem.* 96 (1992) 7485.
- [10] C.V. Ovesen, B.S. Clausen, J. Schiøtz, P. Stoltze, H. Topsøe and J.K. Nørskov, *J. Catal.* 168 (1997) 133.
- [11] N.-Y. Topsøe and H. Topsøe, *Top. Catal.* 8 (1999) 267.
- [12] K.-D. Jung, O.-S. Joo and S.-H. Han, *Catal. Lett.* 68 (2000) 49.
- [13] M.S. Spencer, *Surf. Sci.* 192/193 (1987) 329.
- [14] M. Muhler, L.P. Nielsen, E. Törnqvist, B.S. Clausen and H. Topsøe, *Catal. Lett.* 14 (1992) 241.
- [15] T. Genger, O. Hinrichsen and M. Muhler, *Catal. Lett.* 59 (1999) 137.
- [16] G.C. Chinchen, C.M. Hay, H.D. Vanderwell and K.C. Waugh, *J. Catal.* 103 (1987) 79.
- [17] O. Hinrichsen, T. Genger and M. Muhler, *Chem. Eng. Technol.* 23 (2000) 956.
- [18] H. Bielawa, M. Kurtz, T. Genger and O. Hinrichsen, *Ind. Eng. Chem. Res.* 40 (2001) 2793.
- [19] S.J. Tauster, S.C. Fung and R.L. Garten, *J. Am. Chem. Soc.* 100 (1978) 170.
- [20] J.T. Sun, I.S. Metcalfe and M. Sahibzada, *Ind. Eng. Chem. Res.* 38 (1999) 3868.
- [21] J. Tabatabaei, B.H. Sakakini, M.J. Watson and K.C. Waugh, *Catal. Lett.* 59 (1999) 143.
- [22] B.H. Sakakini, J. Tabatabaei, M.J. Watson and K.C. Waugh, *J. Mol. Catal. A: Chemical* 162 (2000) 297.
- [23] O. Hinrichsen, T. Genger and M. Muhler, *Stud. Surf. Sci. Catal.* 130 (2000) 3825.
- [24] G. Meitzner and E. Iglesia, *Catal. Today* 53 (1999) 433.
- [25] G.C. Chinchen, K.C. Waugh and D.A. Whan, *Appl. Catal.* 25 (1986) 101.