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The temperature-programmed desorption of hydrogen from copper surfaces

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The desorption kinetics of H_2 from a Cu/ZnO/Al_2O_3 catalyst for methanol synthesis were studied under atmospheric pressure in a microreactor set-up by performing temperature-programmed desorption (TPD) experiments after various pretreatments of the catalyst. Complete saturation with adsorbed atomic hydrogen was obtained by dosing highly purified H_2 for 1 h at 240 K and at a pressure of 15 bar. The TPD spectra showed symmetric H_2 peaks centered at around 300 K caused by associative desorption of H_2 from Cu metal surface sites. H_2 TPD experiments performed with different initial coverages resulted in peak maxima shifting to higher temperatures with lower initial coverages indicating that the desorption of H_2 from Cu is of second order. The microkinetic analysis of the TPD traces obtained with different heating rates yielded an activation energy of desorption of 78 $kJ\,mol^{-1}$ and a corresponding frequency factor of desorption of $3 \times 10^{11}\ s^{-1}$ in good agreement with the kinetic parameters obtained with Cu(111) under UHV conditions.

Keywords: Cu/ZnO/Al_2O_3 catalyst, surface area determination, H_2 temperature-programmed desorption (H_2 TPD)

1. Introduction

The temperature-programmed desorption of hydrogen (H_2 TPD) from copper surfaces has been the subject of extensive research over the last two decades [1–7], mainly on single-crystal surfaces. In a detailed study, Anger et al. [4] derived the activation energy for hydrogen desorption under UHV conditions using flash desorption from Cu(111), Cu(110), and Cu(100). On both Cu(100) and Cu(110), adsorbed atomic hydrogen introduces surface reconstruction leading to strongly coverage-dependent kinetic desorption parameters, whereas on Cu(111), H_2 desorption follows second-order kinetics with only weakly coverage-dependent kinetic parameters [4]. From an industrial point of view, the interaction of hydrogen with copper is a significant step in methanol synthesis. The fundamental steps of methanol synthesis were determined in detail by the Topsøe group [8–11]. They presented a mechanism based on surface science studies on single crystals both under UHV and high-pressure conditions [9]. In their latest microkinetic study, the results for the dynamic changes in particle shape and active surface area observed by *in situ* EXAFS were explicitly included in the model in order to predict high-pressure methanol synthesis data over a broad range of partial pressures successfully [10,11]. Using a TPD/IR vacuum cell, Roberts and Griffin measured temperature-programmed desorption spectra of H_2 from various Cu/ZnO-based catalysts prepared by coprecipitation [3]. The H_2 desorption kinetics were analyzed only by the Redhead equation assuming a preexponential factor of $10^{13}\ s^{-1}$. Muhler et al. [7] established the H_2 TPD method as a new tool for the determination of Cu metal surface areas. Compared to the widely used N_2O frontal chromatography [12], the H_2 TPD method turned out to be essentially non-destructive. Recently, Lloyd et al. [13] gave new insight into the surface and bulk interaction of hydrogen with a Cu foil incorporating the results obtained with single-crystal surfaces under UHV conditions.

Nevertheless, the kinetic parameters of H_2 desorption from a Cu/ZnO/Al_2O_3 catalyst under atmospheric pressure have not been derived directly yet. Therefore, in this contribution a detailed kinetic study will be presented using a Cu/ZnO/Al_2O_3 catalyst for methanol synthesis followed by a microkinetic analysis of the TPD data which comprise experiments with varied initial coverages and heating rates. Furthermore, we will provide some new experimental guidelines for the application of the H_2 TPD method as a reliable tool for the determination of Cu metal surface areas.

2. Experimental

The experiments were carried out in an all stainless steel microreactor set-up described in detail in [7] equipped with four gas lines: He (99.9999%), H_2 (99.9999%), a mixture of 72% H_2, 10% CO and 4% CO_2 in He used as methanol synthesis feed gas (99.9995%). The methanol synthesis feed gas was further purified by means of a guard reactor filled with ZnO to adsorb impurities such as sulfur and chlorine compounds. The set-up could be operated at pressures up to 60 bar. Gas analysis was performed by a calibrated quadrupole mass spectrometer (Balzers GAM 400). The kinetic experiments were carried out with a conventional

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ternary $Cu/ZnO/Al_2O_3$ catalyst (approximately 50 wt% Cu) prepared by coprecipitation as described in [14]. 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 19 mm. All experiments were conducted with the same catalyst sample after several weeks on stream. The *ex situ* BET surface area determined after the test series amounted to 35.4 $m^2\,g^{-1}$.

The reduction of the catalyst was carried out carefully with 2% H_2 in He using a heating ramp of 1 K/min up to 513 K following the guidelines given in [14]. The catalytic activity of the reduced catalyst was determined by cycling the temperature between 453 and 513 K using the methanol synthesis feed gas at atmospheric pressure. In this study, synthesis temperatures higher than 513 K were avoided to prevent the catalyst from additional sintering.

The H_2 TPD experiments were carried out according to the following procedure: Methanol synthesis was run prior to each experiment overnight. Then the catalyst was flushed for 1 h in H_2 at 493 K to remove all oxygen-containing adsorbates from the surface. This procedure was chosen in order to achieve a well-defined surface as a starting point for the transient experiments. Then the gas was changed from H_2 to He with subsequent flushing for another hour to remove adsorbed atomic hydrogen followed by cooling in He down to the dosing temperature of 240 K by means of a cryostat. At this temperature no significant desorption of H_2 from the Cu surface has been observed [7]. After dosing H_2 for the specified period of time the catalyst was rapidly cooled down to 78 K with liquid nitrogen. Finally, the gas flow was changed to He in order to flush the catalyst for further 40 min, and then the H_2 TPD experiment was carried out by starting the temperature ramp. The dead volume between the catalyst bed and the mass spectrometer was taken into account by correcting the H_2 TPD traces for a time lag of about 3 s corresponding to a He flow of 100 $\mathrm{Nml\,min^{-1}}$ during all experiments.

3. Results

Figure 1 displays two H_2 TPD traces obtained after dosing pure H_2 under different dosing pressures. The most pronounced feature of both TPD spectra is the narrow symmetric peak centered at about 300 K which can be assigned to H_2 desorption from metallic Cu surface sites. In addition to the main peak at 300 K, a second broad peak is observed with substantially lower intensity at around 410 K. The additional desorption of H_2 is caused by the dissociation of water which originates from impurities of the dosing gas used. This phenomenon may have influenced the experimental results obtained by Bailey and Waugh [15] and will be presented elsewhere in more detail [16]. The slightly decreasing baseline is due to the low pumping speed of H_2 within the mass spectrometer chamber.

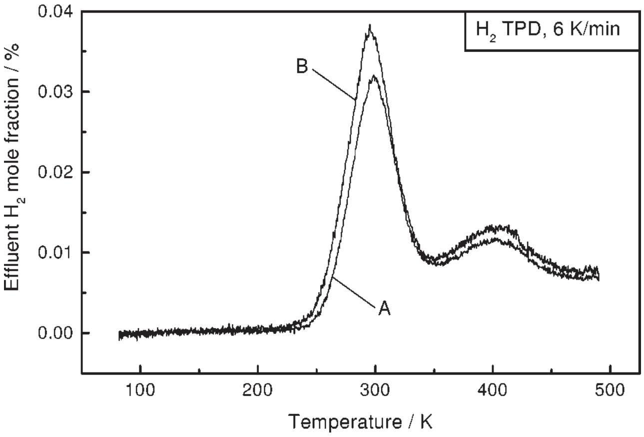

Figure 1. H_2 TPD spectra obtained after dosing pure H_2 at atmospheric pressure (trace (A)) and at 15 bar (trace (B)). Experimental conditions: $Q = 100\ \mathrm{Nml\,min^{-1}}$, $\beta = 6\ \mathrm{K\,min^{-1}}$, $w_{\mathrm{cat}} = 0.2$ g.

Table 1
Amount of H_2 adsorbed and calculated relative coverages corresponding to the TPD traces in figures 2 and 3.

Exposure	Figure	μmol H_2/g_{cat}	Θ_H
1 h, 5800 ppm H_2	3(A)	5.17	0.09
3 h, 5800 ppm H_2	3(B)	10.1	0.18
6 h, 5800 ppm H_2	3(C)	14.5	0.27
2 h, pure H_2 at 1 bar	1(A)	45.8	0.84
1 h, pure H_2 at 15 bar	1(B)	54.6	1

It was possible to reproduce the areas experimentally within 3% which were obtained by integration of the left half of the symmetric peak and multiplication by a factor of 2. The peaks were integrated after subtraction of a linear baseline drawn through the background at the onset of the trace and extrapolated to the end of the high-temperature peak. Using a dosing pressure of 15 bar (figure 1(B)) instead of 1 bar leads to complete saturation with adsorbed atomic hydrogen yielding an amount of exposed Cu surface atoms of 218 μmol/g, which is about 16% larger than the one obtained by dosing H_2 at atmospheric pressure. Due to a higher initial coverage of adsorbed atomic hydrogen the peak maximum is shifted to lower temperatures. Therefore, it is highly recommended to apply high-pressure dosing for the determination of Cu surface areas. The amounts of adsorbed H_2 obtained subsequent to different pretreatments and the corresponding relative coverages are listed in table 1. Taking into consideration that the mean atom density of the low-index planes amounts to $1.47 \times 10^{19}\ m^{-2}$, the resulting Cu surface area is derived to be 8.9 $m^2\,g^{-1}$ as used for the modeling.

The narrow symmetric TPD peak shapes indicate a second-order desorption without readsorption within the catalyst bed. The kinetics of the desorption were studied more detailed by performing H_2 TPD experiments with different heating rates after dosing pure H_2 under atmospheric pressure. The experimental results in figure 2 clearly show that the peak maximum shifts towards higher temperatures with increasing heating rates while the onset of the peaks

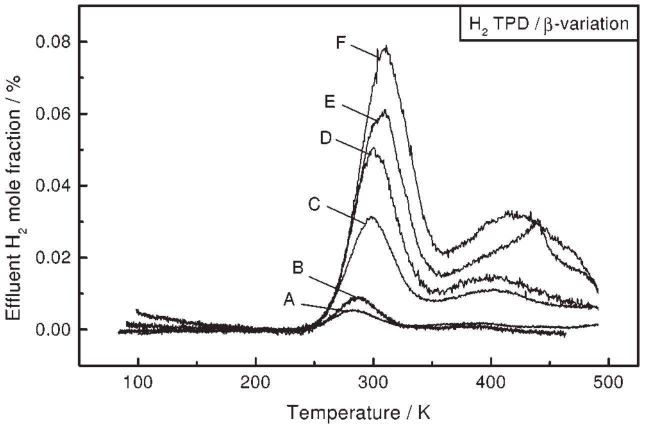

Figure 2. H_2 TPD spectra obtained after dosing pure H_2 at atmospheric pressure using the following heating rates: (A) 1 $\mathrm{K\,min^{-1}}$ ($T_{\max} = 283$ K), (B) 2 $\mathrm{K\,min^{-1}}$ ($T_{\max} = 287$ K), (C) 6 $\mathrm{K\,min^{-1}}$ ($T_{\max} = 299$ K), (D) 10 $\mathrm{K\,min^{-1}}$ ($T_{\max} = 302$ K), (E) 15 $\mathrm{K\,min^{-1}}$ ($T_{\max} = 307$ K), and (F) 20 $\mathrm{K\,min^{-1}}$ ($T_{\max} = 310$ K).

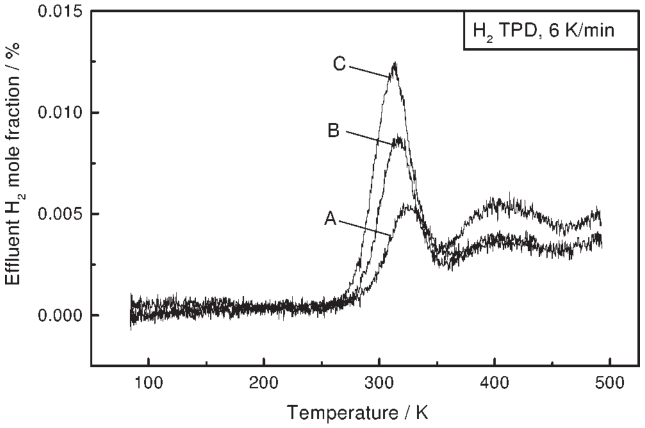

Figure 3. H_2 TPD spectra obtained after exposing the catalyst to a mixture of 5800 ppm H_2 in He for $t = 1$ h (trace (A), $T_{\max} = 325$ K), $t = 3$ h (trace (B), $T_{\max} = 316$ K), and $t = 6$ h (trace (C), $T_{\max} = 313$ K) at atmospheric pressure. A heating rate of $\beta = 6\ \mathrm{K\,min^{-1}}$ was chosen.

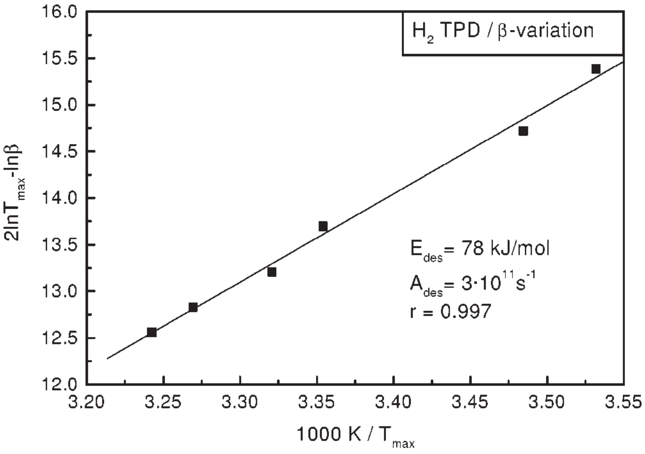

Figure 4. Microkinetic analysis assuming associative desorption without readsorption yields $A_{\mathrm{des}} = 3 \times 10^{11} \pm 1 \times 10^{11}\ \mathrm{s^{-1}}$ and $E_{\mathrm{des}} = 78 \pm 1$ kJ/mol.

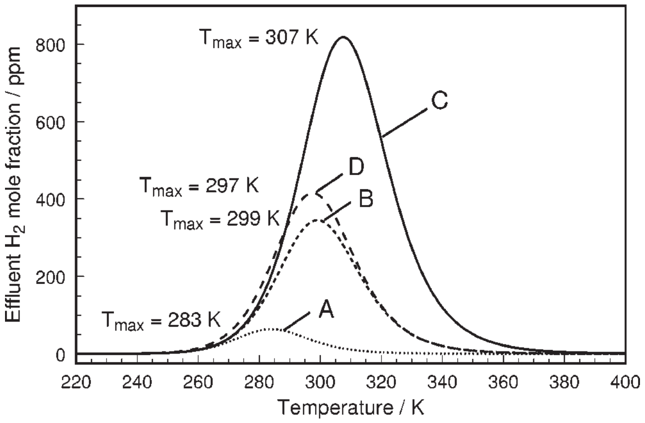

Figure 5. Simulation of three experimental H_2 TPD spectra using $k_{\mathrm{des}} = 3 \times 10^{11}\ \mathrm{s^{-1}} \times \exp[(-78\ \mathrm{kJ/mol})/RT]$ (trace (A), 1 $\mathrm{K\,min^{-1}}$ and $\Theta_{\mathrm{H}} = 0.84$; trace (B), 6 $\mathrm{K\,min^{-1}}$ and $\Theta_{\mathrm{H}} = 0.84$; trace (C), 15 $\mathrm{K\,min^{-1}}$ and $\Theta_{\mathrm{H}} = 0.84$; and trace (D), 6 $\mathrm{K\,min^{-1}}$ and $\Theta_{\mathrm{H}} = 1.0$).

remains at the same temperature of about 250 K. Moreover, the full width at half maximum (FWHM) of 50 K is constant for every peak.

Figure 3 displays the H_2 TPD traces obtained after different dosing times under atmospheric pressure using a diluted mixture of 5800 ppm H_2 in He instead of pure H_2. The peak maximum and the onset of the peak shift towards lower temperatures with increasing dosing time while the high-temperature tails of the TPD traces converge at higher temperatures. Both phenomena are in accordance with Langmuirian second-order desorption kinetics.

The determination of the activation energy of desorption and the corresponding frequency factor is straightforward assuming second-order desorption without readsorption. Plotting $\ln(T^2_{\max}/\beta)$ versus $1/T_{\max}$ results in a straight line as displayed in figure 4. Applying linear regression yields an activation energy (E_{des}) of 78 ± 1 kJ/mol and a preexponential factor (A_{des}) of $3 \times 10^{11} \pm 1 \times 10^{11}\ \mathrm{s^{-1}}$ within the experimental errors assuming a relative coverage of atomic adsorbed hydrogen of 0.84. For the simulation the microreactor has been modeled as a continuous stirred tank reactor (CSTR) combined with the differential equation for the associative desorption written in one step using coverage-independent rate constants k_{i}. As reported from TPD studies on Cu single crystals [4], the saturation coverage of hydrogen on all three low-index planes of Cu is H/Cu = 1/2. Therefore, the corresponding equation for the dissociative adsorption on Cu surfaces is $H_{2(g)} + 4Cu_{(s)} \rightarrow 2(Cu\text{–}H\text{–}Cu)_{(s)}$. In the modeling we used two copper metal surface sites as an active site.

Figure 5 shows the modeling results using the kinetic parameters obtained by the microkinetic analysis of the TPD experiments. The shape and the FWHM of the modeled TPD spectra as well as the positions of the peak maximum are in very good agreement with the obtained experimental data displayed in figures 1 and 2.

4. Discussion

It is well documented in the literature that the dissociative adsorption of hydrogen on copper surfaces is an activated process [4,5,17–19]. Correspondingly, the high symmetry of the experimental TPD peaks presented here indicates that there is no observable readsorption in the catalyst bed during the H_2 TPD experiment which would lead to substantially broadened and shifted TPD peaks. Values for the activation energy of hydrogen desorption from copper have been reported in the literature for several surface morphologies. Anger et al. [4] studied the desorption kinetics under UHV conditions from the three low-index faces of copper, i.e., Cu(100), Cu(110), and Cu(111). On both Cu(100) and Cu(110), adsorbed atomic hydrogen induces surface reconstruction. On Cu(100), the onset of H_2 desorption was found to shift strongly to 200 K, whereas on Cu(110), the TPD peak maximum did not shift to lower temperatures with increasing initial coverages. Both results point to the absence of these planes on the catalyst studied under the pretreatment in H_2 and He described above.

For the Cu(111) surface, the spectrum was found to be fully compatible with second-order desorption with a slight broadening towards higher temperatures, due to adsorbate–adsorbate interactions. Based on the Polanyi–Wigner equation, the evaluation of the desorption spectra for H_2 from Cu(111) by Anger et al. [4] resulted in a coverage-dependent expression. The desorption energy was found to decrease from 77 to 65 kJ/mol with increasing hydrogen coverage (Θ_H) while the preexponential factor decreases from 1.5×10^{11} s^{-1} exponentially with Θ_H based on the model described in [20]. For the Cu(110) surface, they obtained a decrease from 100 to 50 kJ/mol with increasing Θ_H. The value of 50 kJ/mol is consistent with earlier results reported by Wachs and Madix for deuterium desorption from Cu(110) [1]. Due to the surface reconstruction during the H_2 TPD experiment from Cu(100) an evaluation of the flash desorption spectra according to a standard evaluation method is considered to be not feasible [4]. The kinetic parameters obtained in this contribution from our TPD experiments by microkinetic analysis are in good agreement with the ones obtained for experimental data from Cu(111) surfaces [4].

In previous studies on coprecipitated $Cu/ZnO/Al_2O_3$ catalysts, the Griffin group [3,21] also observed a single desorption state in the region of 308–318 K under similar experimental conditions. Using the Redhead equation they derived an apparent activation energy for hydrogen desorption of about 86 kJ/mol and a preexponential factor of 10^{13} s^{-1}. Under the same experimental conditions presented in figure 1 (dosing at 1 bar), Muhler et al. [7] observed the same spectrum using a different $Cu/ZnO/Al_2O_3$ catalyst. It is evident that the peaks observed in the present study can be assigned to desorption from Cu metal surface sites. Since both the kinetic parameters derived by the microkinetic analysis and the TPD peak shapes are in good agreement with those obtained by Anger et al. [4] for Cu(111) it seems safe to conclude that the Cu particles of the $Cu/ZnO/Al_2O_3$ catalyst investigated after the pretreatment described above largely expose Cu(111) surfaces.

Modeling a desorption experiment under the UHV conditions given in [4] with our kinetic parameters yields a symmetric signal with a peak maximum at 324 K and a FWHM of only 48 K. This modeling result can be compared to the TPD results on Cu(111), i.e., a peak at about 310 K with a FWHM of 65 K [4]. The good agreement between experiment and modeling results justifies the application of a simple Langmuir model with coverage-independent kinetic parameters.

The results of the H_2 TPD experiments obtained by varying the dosing time using a diluted mixture of H_2 in He were found to indicate second-order desorption, i.e., shifting of the peak and the onset maximum towards lower temperatures with increasing dosing time. However, the peak maxima obtained by microkinetic modeling are at 321 (for trace (A) in figure 3), 313 and 309 K only in fairly good agreement with the experimental peak positions at 325, 316, and 313 K, respectively. Obviously, for these low coverages the simple Langmuir model overpredicts the experimental outcome slightly.

5. Conclusions

Complete saturation with adsorbed atomic hydrogen was achieved by dosing pure H_2 for 1 h at 240 K and at a pressure of 15 bar. It was shown that the subsequent H_2 TPD experiment is a useful tool for the determination of Cu metal surface sites. The kinetics of associative desorption of hydrogen from a $Cu/ZnO/Al_2O_3$ catalyst were found to follow a second-order rate law. The microkinetic analysis of a series of experiments with different heating rates based on a Langmuir model led to a $k_{des} = 3 \times 10^{11}$ $s^{-1} \times \exp[(-78$ kJ/mol$)/RT]$, which is in good agreement with the one obtained with Cu(111) under UHV conditions.

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