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The coverage-dependent adsorption of carbon monoxide on hydrogen-reduced copper catalysts: the combined application of microcalorimetry, temperature-programmed desorption and FTIR spectroscopy

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Abstract

The strong metal-support interactions occurring in Cu/ZnO catalysts are significantly influenced by the pretreatment. The objective of this contribution is to demonstrate that by carefully reducing binary Cu/ZnO and ternary Cu/ZnO/Al_2O_3 samples in hydrogen under the same conditions, the Cu metal surface is accessible in identical states to adsorption microcalorimetry, TPD experiments and transmission FTIR spectroscopy using carbon monoxide as probe molecule. All techniques show that a fully reduced and clean Cu surface is resulting from a thorough reduction in flowing high-purity hydrogen. The adsorption of CO on this Cu surface is fully reversible at room temperature, with heats of adsorption ranging between 70 kJ/mol at low coverages and 45 kJ/mol at high coverages.

Keywords: Copper; Adsorption; Carbon monoxide; Microcalorimetry; TPD; FTIR

1. Introduction

Copper catalysts are widely used for the industrial methanol synthesis. These catalysts are ternary systems containing copper, zinc oxide and alumina [1]. Several recent studies indicate that there are strong metal-support interactions (SMSI) between copper and zinc oxide in these catalysts. Under the reducing conditions of the methanol synthesis, the metallic copper surfaces are covered by zinc and oxygen species [2]. Under more severe conditions, surface and bulk alloying leads to the formation of brass [3]. The adsorption of CO can be applied as a quantitative tool to investigate the nature of the SMSI effect [4].

In this contribution, three different techniques are used to study the adsorption of CO on copper catalysts, which are linked by the same gas supply and gas analysis units for sample pretreatment. The objective is to demonstrate that by pretreating samples under the same conditions in carefully designed apparatuses, the metallic copper surface is accessible in identical states to microcalorimetry, temperature-programmed desorption (TPD), and transmission Fourier transform infrared (FTIR) spectroscopy. To the best of our knowledge, this is a novel experimental approach to obtain a comprehensive quantitative understanding of the adsorption of CO on Cu/ZnO catalysts.

The heat of adsorption can be derived from TPD experiments using the Redhead equation, or from adsorption isotherms using the Clausius–Clapeyron equation. A more direct approach is to measure the differential heat of adsorption as a function of coverage by adsorption microcalorimetry. The value of this tool for the characterization of catalyst

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surfaces is demonstrated in numerous examples in the literature, focusing, e.g. on acid sites in zeolites or on metal oxide surfaces [5,6]. Spiewak and Dumesic [7] presented a technique, which allows to study reactive catalyst surfaces unimpaired by poisoning. For example, they applied this technique to determine the heat of adsorption of nitrogen on reduced and extremely air-sensitive iron catalysts. Samples were pretreated ex situ in ultra-pure flowing gases, and then sealed in pyrex capsules in inert gas. These capsules were transferred into the calorimeter, and were broken after degassing the microcalorimetric cells. Small doses of the adsorptive gas were subsequently admitted to the adsorbent, and while the heat of adsorption was measured calorimetrically, the amount of adsorbed species was measured volumetrically. A crucial point is the required very low leakage rate of the complete set-up. This procedure prevents the contamination of the sample with oxygen or moisture and yields data of the clean catalyst surface. A further developed version of the adsorption microcalorimetry set-up described in Ref. [7] was used in the work reported here to study the adsorption of CO on copper catalysts as a function of coverage.

The adsorption of CO can be indirectly investigated by TPD experiments using fixed-bed microreactors. For non-activated adsorption, the activation energy of desorption equals the heat of adsorption, as is the case for CO adsorption on metallic Cu surfaces [8]. Consequently, the CO TPD peaks are shifted to higher temperatures due to readsorption within the fixed bed. The coverage dependence of the heat of adsorption can be investigated by varying the initial coverage. In this work, the experiments were carried out with a U-tube reactor monitoring the desorption of CO into a stream of helium by on-line mass spectrometry.

CO is a frequently used probe molecule in FTIR studies. At low coverages, CO adsorbs onto copper surfaces non-dissociatively and linearly in on-top position. The ν(C–O) stretching vibration of adsorbed CO is sensitive to the strength of the bond to the adsorbent, and thus sensitive to the state of reduction of copper. In transmission IR studies, relative coverages can be derived according to the Lambert–Beer law thus allowing to determine adsorption isotherms. In this contribution, the adsorption of CO was investigated using a modified transmission IR cell designed by Karge and Nießen [9]. The pressure of CO was varied stepwise between 0 and 100 Pa in order to investigate the adsorption of CO as a function of coverage.

The interaction of Cu catalysts with hydrogen has been studied extensively by the Bochum group [2,10,11]. The catalysts had been investigated in different states: directly after hydrogen reduction, after a period of 12 h of methanol synthesis, and after a pretreatment of 64 h in CO/He. The same reduction procedure was applied in the present study, and all results refer to the state of the catalysts after hydrogen reduction. The investigated samples are a binary Cu/ZnO catalyst with a molar Cu:Zn ratio of 50:50, an industrial-type catalyst with a molar copper content of 50%, and a ternary catalyst with a molar Cu:Zn:Al ratio of 10:60:30.

2. Experimental

2.1. Adsorption microcalorimetry

The adsorption microcalorimetry set-up consists mainly of three sections: the calorimeter, the microcalorimetric cells and the thermostated volumetric dosing section. A schematic diagram of the set-up is shown in Fig. 1 (left). The calorimeter is a commercially available Tian-Calvet heat-flux microcalorimeter (C80 II, Setaram) which can be operated from

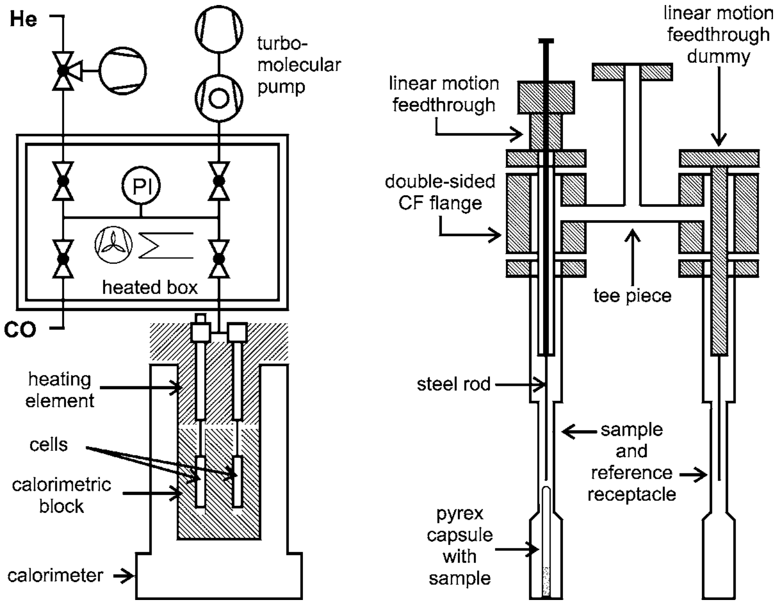

Fig. 1. Flow scheme of the adsorption microcalorimetry set-up.

room temperature up to 573 K. The calorimetric resolution is 0.1 μW, and the detection limit is 2–5 μW. The calorimeter is equipped with a homemade heating element fitted into the upper part of the calorimeter, and specially designed microcalorimetric cells connected to the volumetric dosing section. The heating element keeps all parts of the cells that are not in the calorimetric block or the volumetric dosing section thermostated.

The microcalorimetric cells are shown in Fig. 1 (right). They fit exactly into the calorimeter and the heating element. The cells are designed as symmetrically and simply as possible. The linear motion feedthrough (E-LMD-133-2, Caburn MDC) can be used to crush the pyrex capsules in the sample receptacle via a steel rod. All parts of the cells are made of stainless steel and are UHV-tight (ultra-high vacuum).

The volumetric dosing section is made of four completely metal-tightened bellows valves and a Baratron capacity manometer (range: 0–100 Pa). The complete UHV-tight dosing section is placed in a heated box. The four valves are connected to the microcalorimetric cells, a CO gas line, a helium gas line and a turbomolecular drag pump (TMU 071 P, Pfeiffer). The leakage rate of the set-up including the microcalorimetric cells is less than 10^{-10} Pa m^3/min after degassing for more than 72 h at 423 K. The leakage rate is derived from the observed pressure increase under static vacuum conditions taking the volume of the dosing section and the microcalorimetric cells (approximately 100 cm^3) into account.

Typically, 100 mg of the sieve fraction of 250–355 μm is used for the investigations. Samples are pretreated ex situ in a specially designed pretreatment reactor, and then sealed in a pyrex capsule of 5 mm diameter and 80–90 mm length under a reduced pressure of helium (200–500 hPa). The pyrex capsule is then placed into the sample receptacle of the microcalorimetric cells. The cells are placed into the calorimeter and are connected to the volumetric dosing section. The complete set-up is evacuated at a temperature of 418 K for at least 72 h. This leads to a dynamic vacuum of less than 10^{-5} Pa. After cooling the calorimeter to 303 K and the volumetric dosing section to 313 K overnight, the capsule is broken via the linear motion feedthrough leading to a lowered pressure of the released helium of about 80 Pa. After reaching thermal equilibrium and a steady baseline of the heat flow signal, the adsorption measurement is started. The period of time between the breaking of the capsule and the start of the measurement typically amounts to less than 60 min.

Fig. 2 shows a schematic diagram of the specially designed reactor used for the sample pretreatment. It consists of a glass-lined stainless steel U-tube, a pyrex-metal joint (GA-050P-S, Caburn MDC) with a pyrex NMR tube blown to it, a manometer (−1000 to +2000 hPa, Millipore, not shown), and a four-way valve (4UWE, Valco, VICI). The complete reactor is metal-tightened. Samples are placed into the U-tube and kept in place by a quartz wool plug. The reactor can be heated by a vertically movable heating element. The thermocouple which controls the heating element is fixed onto the outside of the reactor at the position of the sample. The reactor can be connected by Cajon VCR connectors with the flow set-up used for CO TPD experiments (see Section 2.2), which is equipped with a mass spectrometer. The pressure in the reactor may not exceed atmospheric pressure, and the temperature can be raised up to 873 K. After pretreating the sample and purging in helium, the four-way valve of the reactor is closed and the reactor is disconnected from the flow set-up. The heating element is lowered and the reactor is cooled down. In the following step, the pressure of helium in the reactor is decreased to 200–500 hPa using a rotary vane pump (DUO 2.5, Pfeiffer). The reactor itself is then turned vertically by 180°. Thus, the sample falls out of the U-tube into the pyrex tube, while the quartz wool plug stays in the U-tube. Using a small torch fuelled by liquid gas, the pyrex tube is molten to yield a sealed capsule of 80–90 mm length containing the pretreated sample in helium. The sealed capsule is finally placed into the calorimeter.

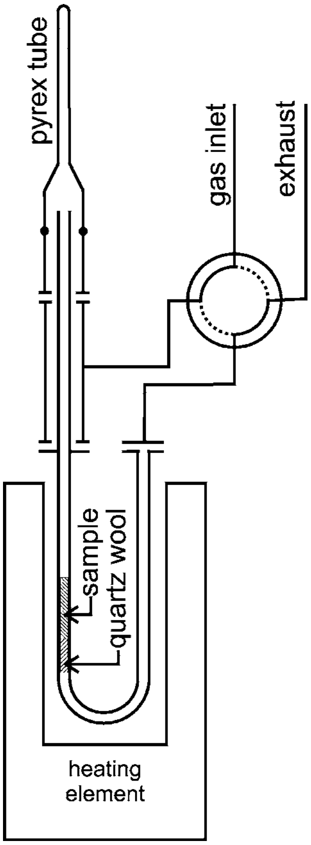

Fig. 2. U-tube reactor used for the pretreatment of microcalorimetric samples.

2.2. CO TPD experiments

The flow set-up used for the pretreatment and the TPD experiments consists of a gas supply unit with seven gas lines, a heated reactor, and a quadrupole mass spectrometer for on-line gas analysis. The reactor is a glass-lined stainless steel U-tube reactor of 3.8 mm inner diameter with two Cajon VCR connectors. The set-up can be operated at pressures of up to 6 MPa and reactor temperatures of up to 873 K. A personal computer equipped with the software package LabView is used to control the set-up. All tubings are made of glass-lined stainless steel to avoid adsorption or reaction of any gas components on the inner tube walls. Tubings between the reactor and the mass spectrometer are heated to a temperature of 366 K to prevent the condensation of products such as water or methanol. The employed gases are helium, a 4% CO_2/He mixture, a 10% CO/He mixture, hydrogen, a 1% N_2O/He mixture, a methanol synthesis gas mixture, and a 2.1% H_2/He mixture. The methanol synthesis gas consists of 72% H_2, 10% CO, 4% CO_2 and 14% He. The gases are all of ultra-high purity (>99.9995%). The gas analysis is performed by an on-line quadrupole mass spectrometer (GAM 400, Balzers) connected via a heated capillary and a tee piece to the exhaust side of the reactor. Data evaluation is performed with the software package Quadstar.

2.3. Transmission FTIR spectroscopy

The FTIR experiments are performed using a Nicolet Nexus FTIR spectrometer equipped with a MCT-A detector. Experiments can be performed in transmission using a further developed IR cell originally designed by Karge and Nießen [9] which is shown in Fig. 3. This IR cell is connected to a sample pretreatment section and a CO dosing system. The cell itself consists of a bronze body soldered to a stainless steel tube of 25 mm diameter. The bronze body is heatable to 403 K and has 9 mm × 18 mm sized openings for the IR beam. The openings are closed by CaF_2 windows of 43 mm diameter sealed with viton O-rings. The sample is positioned into the IR beam in a sample holder made of tantalum which fits exactly into the bronze body. The sample holder can be moved to the pretreatment section by a magnetic manipulator.

All investigations in transmission are carried out using wafers of an area of about 2 cm^2 and a mass of less than 50 mg. The wafers are prepared by grinding powdered samples in an agate mortar, sieving the powder through a piece of cotton fabric directly into the pressing tool, and then pressing the powder for 60 s at a pressure of less than 1 MPa. The resulting wafer is cut to fit into the sample holder, and is transferred into the IR cell. For the pretreatment, the wafer is lifted into the pretreatment section by the magnetic manipulator. It is then pretreated under conditions similar to those of the microcalorimetric and CO TPD experiments. After the pretreatment, the wafer is lowered into the IR beam, and the IR cell is evacuated.

2.4. Investigated samples and pretreatment

The investigated samples are binary and ternary catalysts containing copper, zinc oxide and alumina with the following molar compositions: Cu/ZnO (50:50), Cu/ZnO/Al_2O_3 (50:35:15) and Cu/ZnO/Al_2O_3 (10:60:30). The samples were prepared by coprecipitation using solutions of nitrates and sodium carbonate, followed by aging, washing, drying and calcination. In order to obtain reproducible results, the preparation follows a standardized procedure under controlled conditions (e.g. pH, temperature, reaction and ageing time). The samples were characterized by X-ray diffraction measurements before and after calcination, physisorption measurements (BET surface area), temperature-programmed reduction (copper content), N_2O reactive frontal chromatography (reduced copper surface area), and methanol activity tests. The preparation and the characterization of the samples are described in detail elsewhere [12–14]. The hydrogen reduction is carried out in two steps. The samples are first treated for 12 h in a mixture of 2.1% H_2 in He at 448 K and then for 30 min in pure hydrogen at 513 K using heating rates of 1 K/min. All samples are flushed for at least 30 min at 513 K in flowing helium after the reduction.

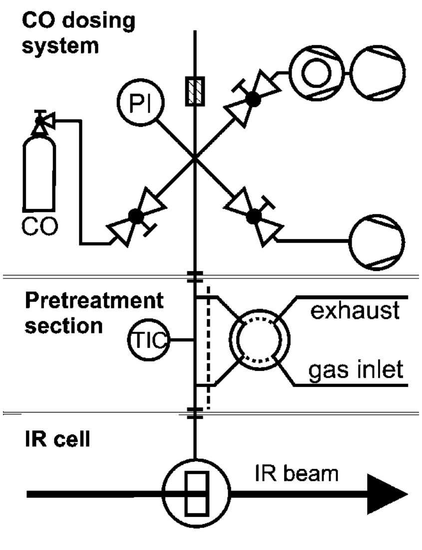

Fig. 3. Flow scheme of the transmission IR cell.

3. Results and discussion

3.1. Calorimetry

Small doses of CO (ca. 1 μmol) are sequentially admitted to the samples to measure the differential heat of adsorption of carbon monoxide, until the saturation of the surface at an equilibrium pressure of ca. 80 hPa is reached. The admission of each dose of CO follows the same cycle consisting of four steps. The first step is the evacuation of the volumetric dosing section to a pressure of less than 10^{-5} Pa, while the valve to the microcalorimetric cells is closed. In the second step, the dosing section is filled with ca. 80 Pa of CO. The admission of

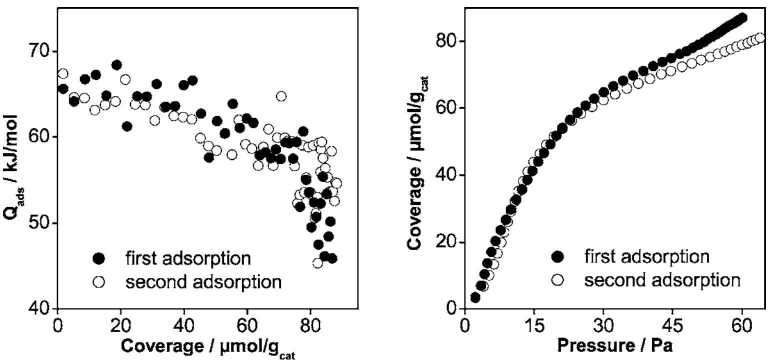

Fig. 4. Differential heat of adsorption (left) and adsorption isotherms (right) of CO on Cu/ZnO (50:50) determined at 300 K.

CO into the microcalorimetric cells is step three. The fourth step is to observe the heat flow and the pressure drop for 1 h. A complete experiment can consist of up to 50 cycles. The differential heat of adsorption and the adsorption isotherm can be derived from the experimental data. For each cycle, the evolved heat is determined by integrating the measured heat flow, and the amount of the adsorbed CO is determined from the measured pressure drop using the universal gas equation. The volume of the dosing section is constant and was determined by the expansion of He into a calibration chamber. The volume of the microcalorimetric cells changes with the position of the linear motion feedthrough and the sample volume. This volume was measured after each experiment by the expansion of He into the evacuated microcalorimetric cells.

To distinguish between reversible and irreversible adsorption, the complete set-up is evacuated overnight without raising the temperature. After filling the microcalorimetric cells with ca. 80 Pa of helium and reaching a steady baseline of the heat flow signal, the adsorption experiment is repeated. Any differences between the first and the second adsorption experiment are related to irreversible adsorption. In total, one experiment can last up to 1 week. This explains why the leakage rate of the set-up has to be less than 10^{-10} Pa m^3/min.

Fig. 4 shows the results of the CO adsorption experiments on the reduced binary Cu/ZnO catalyst (50:50). Integration of the mass spectrometry traces confirmed the complete reduction of copper. The differential heat of adsorption is found to decrease almost linearly from 68 kJ/mol at very low coverage to 57 kJ/mol at a coverage of about 80 μmol$_{CO}$/g$_{cat}$, followed by a steep decrease to nearly 45 kJ/mol. The saturation coverage of the binary catalyst with CO was about 90 μmol$_{CO}$/g$_{cat}$ at a pressure of 60 Pa. The low initial value of the heat of adsorption confirms the absence of Cu(I) species and the complete reduction of copper [15]. There are only negligible differences between the first adsorption experiment and the second one after evacuation at room temperature, indicating that the adsorption of CO is fully reversible under these conditions. This is evident both from the differential heat as well as from the adsorption isotherms shown in Fig. 4. The repeated adsorption experiment also shows that the ongoing contamination of the sample with air by leakage is without measurable effect.

The adsorption of CO on the ternary catalysts was also found to be reversible in agreement with Ref. [4], in which microcalorimetric results of CO adsorption on Cu/Al$_2$O$_3$ (85:15), Cu/ZnO (70:30) and Cu/ZnO/Al$_2$O$_3$ (50:35:15) samples pretreated by hydrogen reduction were presented. The differential heat of adsorption of CO on Cu/ZnO/Al$_2$O$_3$ (50:35:15) ranged from 68 to 50 kJ/mol with a saturation coverage of ca. 85 μmol$_{CO}$/g$_{cat}$ [4]. Thus, following the argumentation of Cardona-Martinez and Dumesic in Ref. [16], reversibility had been expected. The adsorption isotherms can be further analyzed by simple models such as the Temkin or Freundlich isotherm. This will be shown elsewhere [17].

3.2. CO TPD results

For CO TPD experiments with the ternary catalyst (10:60:30), 100 mg of the sieve fraction of 250–355 μm are used. After the catalyst pretreatment, CO is adsorbed at 300 K in a flowing mixture of CO in He (10% CO, 10 Ncm^3/min). The sample is then cooled to 78 K rapidly in flowing CO/He by pouring liquid nitrogen into the heating block. It is purged with pure He (10 N cm^3/min) for 10 min and then heated to 450 K with a heating rate of 6 K/min in flowing helium. The effluent mole fraction of CO is monitored by the mass spectrometer. This procedure yields the CO TPD data from the fully covered catalyst surface. To vary the initial coverage of the CO TPD experiments, the catalyst samples are heated to 450 K in two steps, e.g. the sample is first heated to 275 K, again cooled to 78 K, and then heated to 450 K. In the first step, the weakly bound CO species desorbing in the temperature range up to 275 K are removed. The final temperature of the first step defines the initial surface coverage of the second step. In order to investigate the influence of the coverage on the desorption, the complete experiment is repeated at different final temperatures of the first step ($T_{\text{first step}}$). Typical temperatures are 275, 300, 325, and 350 K. This technique leads to surface coverages of CO which are comparable to the coverages obtained in the microcalorimetric experiments (Table 1).

Fig. 5 shows the results of the experiments with varying initial surface coverage. The characteristics of the four peaks (a)–(d) are summarized in Table 1. The final temper-

Table 1
CO TPD data obtained with Cu/ZnO/Al_2O_3 (10:60:30)

Peak	$T_{\text{first step}}$ (K)	$T_{\max}$ (K)	FWHM (K)	Coverage ($\mu mol_{CO}/g_{cat}$)	Fractional coverage	ΔH_{ads}^{TPD} (kJ/mol)	ΔH_{ads}^{exp} (kJ/mol)
a	275	308	82	26.8	0.20	–[a]	
b	300	328	64	18.7	0.14	56.5	56.4[b]
c	325	344	48	8.0	0.06	59.2	61.2[b]
d	350	355	42	2.3	0.02	61.1	64.7[b]

ΔH_{ads}^{exp} is the integral molar heat of the adsorption of CO on Cu/ZnO/Al_2O_3 (50:35:15) derived from the microcalorimetric data in [4].

[a] Not available.

[b] Measured for the corresponding fractional coverage.

ature of the first heating step is $T_{\text{first step}}$. The temperature of the absolute peak maximum is $T_{\max}$. The peak maxima are shifted by more than 100 K to higher temperatures, compared with the results of a thermal desorption spectroscopy (TDS) study in UHV by Vollmer et al. [8]. These experiments included low- and high-indexed copper single crystal surfaces and polycrystalline copper. The temperature shift between experiments using single crystals and fixed catalyst beds is due to readsorption occurring in the catalyst bed. The full width at half maximum (FWHM) is also summarized in Table 1. The TPD peaks are asymmetric to lower temperatures, indicating a first order desorption process, and are broadened by readsorption. An additional broadening of the largest peak (Fig. 5a) is due to contributions from a second desorption site occupied at lower temperatures. The initial coverages are calculated by integrating the mass spectrometry traces over the complete range of the desorption peak. ΔH_{ads}^{TPD} designates a rough estimate of the heat of adsorption based on the results of the TPD experiments. The estimation follows the method of Konvalinka and Scholten [18], as applied by Sandoval and Bell [19] in a study of the adsorption of CO on Cu/SiO_2. ΔH_{ads}^{TPD} is derived using standard values for the preexponential factors of adsorption and desorption ($10^1\ Pa^{-1}\ s^{-1}$ and $10^{13}\ s^{-1}$, respectively) given by Dumesic et al. [20]. The values of ΔH_{ads}^{TPD} are just slightly lower than ΔH_{ads}^{exp}, the integral molar heat for corresponding coverages calculated from the microcalorimetric data in [4], thus confirming the decrease of the heat of adsorption with increasing coverage obtained by microcalorimetry.

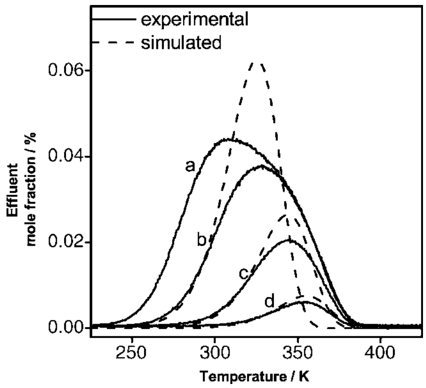

Fig. 5. CO TPD spectra obtained with Cu/ZnO/Al_2O_3 (10:60:30) with varying initial coverage of CO, $T_{\text{first step}}$: (a) 275 K, (b) 300 K, (c) 325 K, and (d) 350 K. The included simulated TPD traces were calculated using the calorimetric data obtained with Cu/ZnO/Al_2O_3 (50:35:15) [4].

It can be safely assumed that the TPD experiments are carried out under thermodynamically controlled near-equilibrium conditions. This assumption is based on the following arguments: the desorption is very fast (see Section 3.3), there is non-activated readsorption over the length of the catalyst bed, and the heating rate of the experiments is sufficiently moderate. The presence of thermodynamic control is confirmed by the good agreement between the experimental and the simulated TPD traces (b)–(d) shown in Fig. 5 as dashed lines. The latter were obtained using the calorimetric data obtained with Cu/ZnO/Al_2O_3 (50:35:15) [4]. Further details of the modelling of the peaks using the integral molar heat of adsorption measured by microcalorimetry and considering readsorption are to be found in Ref. [17]. The modelling intends to validate the data obtained by the different investigation methods.

3.3. FTIR spectroscopy

The industrial-type ternary catalyst (50:35:15) has a very low transparency in the mid-IR region when completely reduced due to its high copper content. Therefore, a ternary catalyst system (10:60:30) with a lower copper content was investigated in the transmission FTIR experiments using a wafer of ca. 45 mg. The sample was pretreated by hydrogen reduction, and the reduction of copper to its zero valent state was qualitatively confirmed by mass spectrometry. After the IR cell had been cooled down to room temperature, a single beam spectrum was recorded under dynamic vacuum conditions. This spectrum served as background spectrum for the adsorption experiment. The background spectrum was recorded with 2000 scans at a resolution of $2\ cm^{-1}$. The surface coverage of the sample with CO was then increased in steps by increasing the partial pressure of CO stepwise. At each pressure step, a spectrum with 500 scans at a resolution of $2\ cm^{-1}$ was recorded. Typically, the pressure steps were 0, 0.5, 1, 2.5, 5, 10, 20, 40, 80, and 100 Pa. A period of 10 min between each CO dosing and the recording of the spectrum ensured near-equilibrium adsorption/desorption conditions. After recording the spectrum at 100 Pa pressure of CO, the cell was evacuated and two spectra were recorded after 1 min (250 scans) and 10 min (2000 scans).

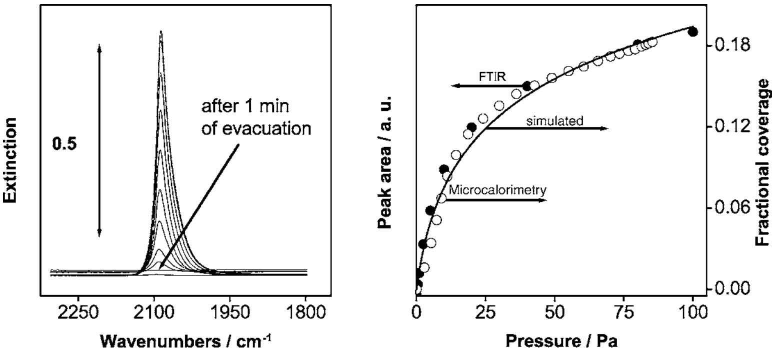

Fig. 6. FTIR spectra obtained with $Cu/ZnO/Al_2O_3$ (10:60:30) (left) and adsorption isotherms of CO (right) obtained with $Cu/ZnO/Al_2O_3$ (10:60:30) (FTIR-based) and $Cu/ZnO/Al_2O_3$ (50:35:15) [4] determined in the pressure range of 0–100 Pa at room temperature. The included simulated adsorption isotherm is based on the microcalorimetric results obtained with $Cu/ZnO/Al_2O_3$ (50:35:15) and a modified Temkin model.

Fig. 6 (left) shows the CO stretching vibration in the region 1900–2300 cm^{-1} during the adsorption of CO in the pressure range 0–100 Pa. Only one broad and asymmetric band with a peak maximum shifting from 2090 to 2086 cm^{-1} with increasing coverage is observed. This band is identified as the stretching vibration of CO adsorbed on metallic copper [21]. The band becomes broader and more asymmetric with increasing coverage. It is found to decrease instantaneously when the cell is evacuated, i.e., the band is no longer visible in the spectrum recorded 1 min after evacuation.

An adsorption isotherm with arbitrary units for the amount of adsorbed CO can be derived from the IR data by integrating the peak areas (Fig. 6, right). The adsorption isotherm of the industrial-type ternary catalyst measured by microcalorimetry is included for comparison [4]. The shape of the FTIR-derived adsorption isotherm of the ternary catalyst (10:60:30) fits well to the adsorption isotherm of the industrial-type catalyst obtained by microcalorimetry. While the absolute coverages ($\mu mol_{CO}/g_{cat}$) are surely different for the two catalysts, the fractional coverages ($\mu mol_{CO}/\mu mol_{Cu,surface}$) appear to follow the same adsorption isotherm, as further supported by the good agreement with the simulated adsorption isotherm derived from the microcalorimetric results obtained with $Cu/ZnO/Al_2O_3$ (50:35:15) and a modified Temkin model. These observations confirm that the copper surfaces of the two ternary catalysts are in the same state after the hydrogen reduction pretreatment.

4. Conclusions

The microcalorimetric results demonstrate the efficiency of the applied technique for the sample transfer into the calorimeter without contamination by air. The results also show that the leakage rate of the microcalorimetry set-up is sufficiently low to investigate the air-sensitive copper surfaces of the reduced samples for several days.

The CO TPD data confirm the microcalorimetry results quantitatively. Similar surface coverages were obtained by both investigation methods. The decrease of the heat of adsorption with increasing coverage measured by microcalorimetry is also observed in the TPD experiments.

The results obtained by FTIR spectroscopy support the conclusions of the microcalorimetric experiments: copper is completely reduced to its zero valent state after thorough hydrogen reduction even under the non-ideal flow conditions of the IR cell, and the adsorption of CO is fully reversible at room temperature. The adsorption isotherms obtained by the two different investigation methods fit well to each other. The results prove that the FTIR set-up is suitable to investigate air-sensitive reduced copper samples unimpaired by oxygen poisoning.

Thus, the three different investigation methods were successfully combined by applying identical pretreatment conditions in well designed apparatuses. The obtained results will be further validated by a microkinetic analysis of the isotherms and the TPD data based on the coverage-dependent heats of adsorption.

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