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THE BACK-TITRATION OF CHEMISORBED ATOMIC OXYGEN ON COPPER BY CARBON MONOXIDE INVESTIGATED BY MICRO-CALORIMETRY AND TRANSIENT KINETICS

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The back-titration of atomic oxygen chemisorbed on metallic copper using carbon monoxide is investigated by microcalorimetry. Results from simulations based on a microkinetic model of the back-titration are used for processing of microcalorimetric data. In addition, surface oxidation of copper by nitrous oxide is investigated by microcalorimetry. The results are compared with results obtained by nitrous oxide reactive frontal chromatography and by static oxygen adsorption studied by microcalorimetry. The heat of adsorption of nitrous oxide on copper amounts to 304 kJ mol^{-1}, and the heat of adsorption of carbon monoxide on surface-oxidized copper is in the range from 120 to 70 kJ mol^{-1}.

Keywords: *adsorption microcalorimetry, carbon monoxide, copper, methanol synthesis, nitrous oxide*

Introduction

Methanol is one of the most important products synthesized industrially. The catalyst applied for the synthesis of methanol is a ternary system containing copper (Cu), zinc oxide (ZnO), and alumina (Al_2O_3) [1, 2]. Although this catalyst has been used during the last four decades and in spite of the importance of methanol synthesis, the nature of the active site and the mechanism of the methanol synthesis are still under debate.

The active site is described e.g. as metallic copper, isolated Cu(I) ions in the ZnO matrix, Cu(I) species stabilized by Cu–Zn alloys, the Cu/ZnO interface, or strained copper particles [3–9]. Results presented by Muhler *et al*. [10–14] indicate that under conditions of methanol synthesis copper is completely reduced to a zero-valent state, the surface of the metallic copper particles is not covered by significant amounts of atomic oxygen and strong metal-support interactions (SMSI) exist between copper and zinc oxide.

Askgaard *et al*. [15] presented a detailed kinetic model for the synthesis of methanol over copper catalysts based on surface science studies. Following their model methanol is synthesized from carbon dioxide only. Adsorbed carbon dioxide is hydrogenated to methanol and water via formate as stable intermediate. The model includes the water-gas shift reaction of carbon monoxide and water. One of the elementary reaction steps on the copper surface is the reaction of adsorbed carbon monoxide with adsorbed atomic oxygen.

Hinrichsen *et al*. [16] studied the chemisorption of nitrous oxide (N_2O) and hydrogen (H_2) for the determination of the free copper surface area of copper catalysts. The authors were able to show that N_2O reactive frontal chromatography (N_2O RFC) carried out under carefully chosen conditions resulted in the formation of a complete monolayer of chemisorbed atomic oxygen without bulk oxidation of copper.

In the present contribution, the surface reaction of CO with atomic oxygen preadsorbed on the surface of supported copper particles is studied by adsorption microcalorimetry and transient kinetics.

Experimental

Samples

The investigated samples are a ternary and a binary catalyst containing copper, zinc oxide and alumina: $Cu_{50}ZnAl$ and $Cu_{75}Al$. $Cu_{50}ZnAl$ is a catalyst of industrial interest with a nominal content of 50% Cu. $Cu_{75}Al$ is a model catalyst with a Cu content of 75%.

The samples are prepared by coprecipitation using solutions of nitrates and sodium carbonate, followed by aging, washing, drying and calcination. The catalysts are characterized by nitrogen physisorption measurements (BET surface area), temperature-programmed reduction (copper content), and N_2O RFC (reduced copper surface area). The preparation and the characterization of the samples are described in detail elsewhere [16–18].

Table 1 summarizes the main characteristics of the used samples.

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Table 1 Characterization of Cu catalysts

Sample	$Cu_{50}ZnAl$	$Cu_{75}Al$
Cu content/mass% CuO[a]	47	76
BET surface area/$m^2\ g_{cat}^{-1}$ [b]	73	51
Cu surface atoms/μmol g_{cat}^{-1} [c]	513	176
Specific Cu surface area/$m_{Cu}^2\ g_{cat}^{-1}$ [d]	21	7

All samples are prepared by coprecipitation from nitrates using sodium carbonate. [a]determined by TPR (100 mg, 2% H_2/He, *rT* to 513 K, 1 K min^{-1}). [b]determined by N_2 physisorption (after evacuation for 2 h at 373 K). [c]determined by N_2O RFC (*rT*, 1% N_2O/He). [d]assuming that 1 m^2 of Cu surface area equals 24.41 μmol of Cu atoms

Pretreatment

The sample pretreatment is carried out ex situ in a flow set-up using a specially designed pretreatment reactor. Samples of 100 mg of the sieve fraction of 250–355 μm are activated by reduction in H_2. The samples are first treated for 12 h in a mixture of 2% H_2 in He at 448 K and then for 30 min in pure H_2 at 513 K. After the reduction and flushing for at least 30 min at elevated temperatures in a flow of pure helium the samples are cooled to room temperature. Heating rates are fixed to 1 K min^{-1}, flow rates are fixed to 10 $cm^3\ min^{-1}$ (STP). The process of reduction is monitored by on-line mass spectrometry.

A detailed description of the used apparatuses, the applied techniques, and the experimental conditions is given elsewhere [12].

Microcalorimetry

The set-up used for the microcalorimetric experiments is based on the pioneering work by Spiewak and Dumesic [19]. It consists of a Tian-Calvet type microcalorimeter (C 80 II, Setaram) and a thermostated volumetric dosing section. Small amounts of the adsorptive gas (e.g. N_2O or CO) are admitted subsequently to the sample, and while the heat is measured calorimetrically, the amount of adsorbed species is obtained volumetrically (not possible in the case of N_2O). The adsorption experiments are carried out in the pressure range of 0–100 Pa under near-equilibrium conditions yielding the adsorption isotherm in addition to the differential heat of adsorption.

After pretreatment the samples are sealed in pyrex capsules under an atmosphere of inert gas. After transfer into the calorimeter and degassing, the capsules are crushed, and the samples are studied unimpaired by oxygen poisoning.

The complete calorimetric investigation of a sample consists of five parts. In the first part, the complete reduction of Cu and the absence of oxygen species on the Cu surface is probed by CO adsorption. At the end of this part the adsorbed CO is removed by evacuation overnight at room temperature. The results of the CO adsorption can be directly compared to already published results [12, 13]. In the second part, the Cu surface is oxidized by dissociative adsorption of N_2O. As one N_2 molecule is released into the gas phase for each N_2O molecule adsorbing on the Cu surface, the uptake of O_{ads} cannot be determined volumetrically. The only available information is the amount of N_2O that is admitted to the sample in each dose of adsorptive gas. Again, the sample is evacuated overnight at room temperature after the adsorption experiment. The third part is the back-titration of the preadsorbed O_{ads} by adsorption of CO. Calorimetric and volumetric data can be collected during this part of the investigation. After evacuation overnight at room temperature the CO adsorption experiment of the first part is repeated for comparison. The comparison is made to test for the complete reversal of the oxidation by back-titration. The last part of the investigation is the adsorption of O_2 (carried out after evacuation overnight at room temperature), also for comparison only.

Transient kinetics

The kinetics of the back-titration can be derived from the volumetric data collected during the back-titration part of the microcalorimetric investigation. While the near-equilibrium pressure of the adsorptive gas measured at the end of each dose and the integrated heat flow measured during the complete dose are relevant for the determination of the differential heat of adsorption and the adsorption isotherm, the change of pressure as a function of time measured during each dose represents kinetic data, in an isothermal batch reactor.

In order to derive kinetic information a simulation of the pressure as a function of time is fitted to the experimental pressure data using a microkinetic model and the software MATLAB. Four elementary steps are needed for a simple model of the back-titration. In the first step, CO adsorbs on an empty adsorption site on the copper surface with the reaction rate r_1 (Eq. (1)). k_{a1} is the rate constant of the adsorption, p_{CO} is the partial pressure of CO, θ_{Cu} is the fraction of free Cu surface atoms, k_{d1} is the rate constant of the desorption, and θ_{CO} is the fractional coverage of the Cu surface with CO.

$$CO + {}^* \leftrightarrows CO^*$$

$$r_1 = k_{a1} p_{CO} \theta_{Cu} - k_{d1} \theta_{CO} \qquad (1)$$

In the second step, CO adsorbed on Cu and O adsorbed on Cu form CO_2 adsorbed on Cu via a surface reaction with the reaction rate r_2 (Eq. (2)). k_2 is the rate constant of the surface reaction, and θ_O is the fractional coverage of the Cu surface with atomic oxygen.

$$\begin{gathered} CO^* + O^* \rightarrow CO_2^* \\ r_2 = k_2 \theta_{CO} \theta_O \end{gathered} \tag{2}$$

The desorption of CO_2 from Cu is the third step. In surface science studies the binding energy of CO_2 on Cu(100) single crystal surfaces is determined to be below 30 kJ mol^{-1}, and accordingly desorption of CO_2 from Cu(100) occurs below 100 K in temperature-programmed desorption experiments [20, 21]. As CO_2 is only weakly bound to metallic Cu, the desorption rate is essentially equal to the formation rate, and readsorption of CO_2 can be neglected under the applied temperature and pressure conditions. The third step is therefore not included in the mathematical model. The last step to be considered is the adsorption of CO_2 on the oxidic support material with the reaction rate r_4 (Eq. (3)). k_{a4} is the rate constant of the adsorption, p_{CO_2} is the partial pressure of CO_2, k_{d4} is the rate constant of the desorption, and θ_{CO_2} is the fractional coverage of the support surface with CO_2.

$$CO_2 + {}^{\#} \leftrightarrows CO_2^{\#}$$

$$r_4 = k_{a4} p_{CO_2} (1 - \theta_{CO_2}) - k_{d4} \theta_{CO_2} \tag{3}$$

Based on Eqs (1)–(3), the following set of differential equations can be derived and used for the kinetic simulation:

$$\frac{d\theta_{CO}}{dt} = r_1 - r_2 \tag{4}$$

$$\frac{d\theta_O}{dt} = -r_2 \tag{5}$$

$$\frac{d\theta_{Cu}}{dt} = -r_1 + 3r_2 \tag{6}$$

$$\frac{d\theta_{CO_2}}{dt} = r_4 \tag{7}$$

$$\frac{dp_{CO}}{dt} = -\frac{r_1 n_{Cu} RT}{V} \tag{8}$$

$$\frac{dp_{CO_2}}{dt} = \frac{(r_2 n_{Cu} - r_4 n_{sup})RT}{V} \tag{9}$$

t is the time, n_{Cu} is the amount of Cu surface atoms, n_{sup} is the amount of adsorption sites for CO_2 on the support material, R is the universal gas constant, T is the temperature, and V is the volume of the microcalorimetric measuring cell.

Results and discussion

The microcalorimetric results obtained during the adsorption of N_2O are shown in Fig. 1. In the case of N_2O adsorption, the amount adsorbed during a pulse cannot be determined volumetrically. Therefore, the diagram shows the evolved heat divided by the amount admitted in each dose, respectively, *vs*. the total amount of admitted N_2O. For both investigated samples similar profiles are obtained. In the beginning, a linear decrease of the evolved heat in the range of about 300–150 kJ mol^{-1} is observed. After a sharp decrease only values below 50 kJ mol^{-1} are measured during further doses of N_2O. The decrease occurs in the range of 100–115 and 325–355 μmol g_{cat}^{-1} for the samples $Cu_{75}Al$ and $Cu_{50}ZnAl$, respectively. This difference can be rationalized by the fact that the specific copper surface area of $Cu_{50}ZnAl$ is about three times larger than the specific copper surface area of $Cu_{75}Al$. A straightforward explanation for the decrease of the evolved heat is the saturation of the copper surface with atomic oxygen, i.e. the formation of a monolayer of Cu_2O.

This explanation is supported by the results obtained during the oxygen adsorption carried out in the last step of the microcalorimetric experiment. Figure 2 shows the differential heat of adsorption and the adsorption isotherm of O_2 on $Cu_{50}ZnAl$. An important difference between the adsorption of O_2 and the adsorption of N_2O is the fact that the adsorbed amount of O can be determined volumetrically during the O_2 adsorption experiment. In the beginning of the O_2 adsorption experiment in the range 0–200 μmol g_{cat}^{-1}, a constant heat of adsorption of 195 kJ mol^{-1} is measured. A sigmoidal decrease of the heat of adsorption from 195 to 135 kJ mol^{-1} is observed in the range of about 200–320 μmol g_{cat}^{-1} of adsorbed O. The

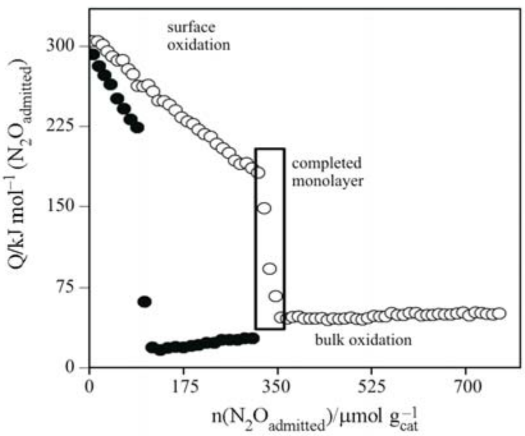

Fig. 1 Heat of adsorption of N_2O on $Cu_{50}ZnAl$ (hollow symbols) and $Cu_{75}Al$ (filled symbols): evolved heat (related to admitted amount) *vs*. total amount of admitted N_2O

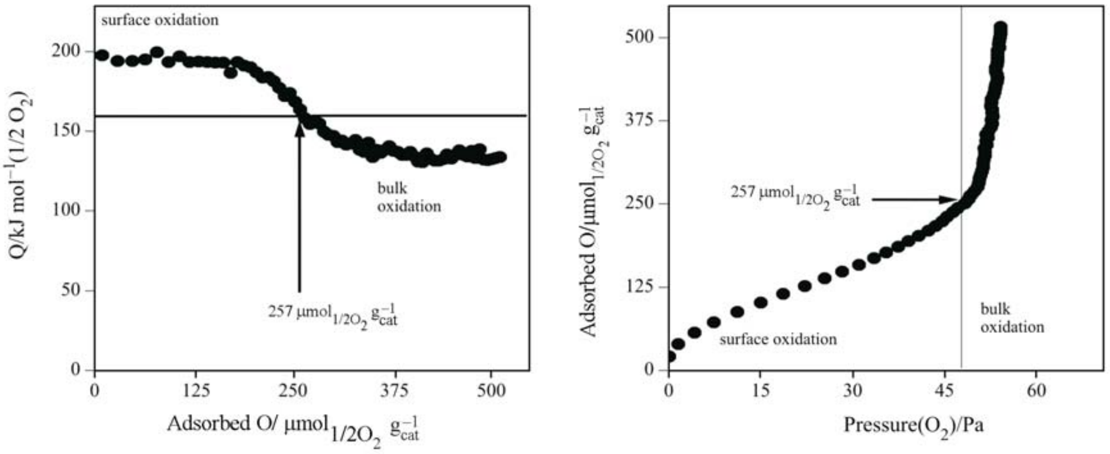

Fig. 2 Differential heat of adsorption and adsorption isotherm of oxygen on Cu$_{50}$ZnAl at 303 K. Surface and bulk oxidation can be clearly distinguished. The results obtained by N$_2$O RFC indicate that a complete monolayer of chemisorbed atomic oxygen is formed at 257 µmol g$_{cat}^{-1}$

inflection point of the decrease is in very good agreement with the value obtained for a monolayer of Cu$_2$O obtained by N$_2$O RFC (257 µmol g$_{cat}^{-1}$ O on 513 µmol g$_{cat}^{-1}$ Cu surface atoms). The measured heat of adsorption is constant at 135 kJ mol^{-1} for adsorbed amounts higher than 320 µmol g$_{cat}^{-1}$. The measured adsorption isotherm indicates that also at low coverage a residual oxygen pressure is present at the end of each dose. The adsorbed amount increases nearly linearly with the partial pressure of O$_2$ until saturation of the copper surface with atomic oxygen at 257 µmol g$_{cat}^{-1}$. After reaching saturation, the adsorbed amount increases still linearly with pressure, however with a significantly steeper slope.

The measured heats of adsorption are in reasonable agreement with the standard enthalpy of formation of Cu$_2$O (–168.6 kJ mol^{-1} [22]). The fact that the measured heat of adsorption is higher for the first monolayer can be rationalized by a higher reactivity of the surface compared to the bulk due to coordinative unsaturation of the surface atoms. The too low value measured for bulk oxidation can be explained with the formation of imperfect crystals as the standard state of a crystal implies perfect symmetry.

In good agreement, Giamello *et al.* [23] reported in a microcalorimetric study a constant value of 181 kJ mol^{-1} for the heat of adsorption of oxygen on Cu/ZnO catalysts. The authors observed a decrease of the heat of adsorption, too, however to much lower values of 80–30 kJ mol^{-1}. The authors also mention a residual oxygen pressure found even at the very initial stage of oxidation. In the same study, the authors report a value of 317 kJ mol^{-1} for the heat of adsorption of N$_2$O on Cu/ZnO samples. They found that the heat of adsorption is not influenced by the coverage and that each dose of N$_2$O is completely

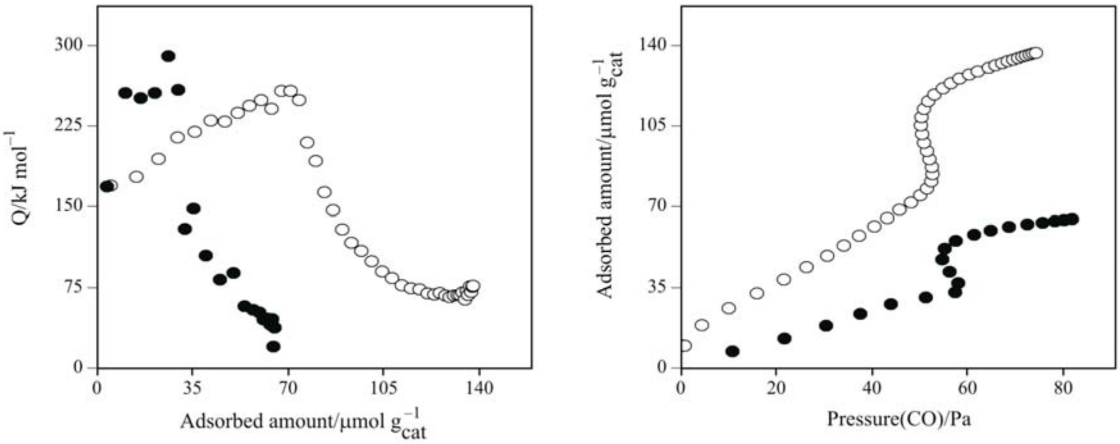

Fig. 3 Results obtained for the differential heat and the adsorption isotherm of CO on Cu with preadsorbed oxygen by straightforward processing of the microcalorimetric data (Cu$_{50}$ZnAl: hollow symbols; Cu$_{75}$Al: filled symbols). The profiles of the differential heat and the adsorption isotherm cannot be related to adsorption, only, and clearly indicate the occurrence of additional processes

consumed until the Cu surface is saturated. The fractional coverage of the Cu surface with atomic oxygen at saturation is given as 0.3.

Taking all information mentioned above into account, the microcalorimetric raw data obtained during the adsorption of N_2O can be processed in two ways. To estimate the total amount of N_2O that is adsorbed until saturation of the copper surface with atomic oxygen is reached, either a constant heat of adsorption or complete consumption of each dose of N_2O can be considered. Considering complete consumption of each dose leads to a value of about 330 μmol g^{-1}_{cat} of adsorbed O and would mean that the heat of adsorption is strongly coverage-dependent. On the other hand, considering a constant heat of adsorption of 304 kJ mol^{-1} (the initial value at zero coverage) leads in very good agreement with the N_2O RFC results to a value of about 260 μmol g^{-1}_{cat} of adsorbed O. As a consequence, an increasing residual pressure of N_2O has to be considered. Based on the very good agreement with the N_2O RFC results and the fact that a residual pressure of the adsorptive gas is found even in the case of the more reactive oxygen, we conclude that the heat of adsorption of N_2O is constant, that a complete monolayer of Cu_2O is formed at saturation, and that bulk oxidation by N_2O occurs only to a very low degree.

Bolis *et al.* [24] presented a microcalorimetric study on the chemisorption of CO on fully and partially oxidized Cu/ZnO samples. No further processes except the adsorption of CO were needed for the processing of their data. In the present study, a straightforward processing of the microcalorimetric raw data measured during the back-titration of the chemisorbed oxygen with CO considering only chemisorption of CO on Cu_2O leads to no comprehensible results (Fig. 3). The profiles of the differential heat and the adsorption isotherm clearly indicate the occurrence of additional processes. The pressure data recorded during each dose of CO confirm the presence of these additional processes. Figure 4 shows the pressure data recorded during several CO doses of the back-titration experiment using $Cu_{75}Al$. A simulated pressure profile for a fast and non-activated adsorption process based on the Lagergren equation is included. The experimental pressure profiles can be qualitatively understood considering the microkinetic model given above for the back-titration experiment. A fast pressure drop at the beginning of each dose is related to the adsorption of CO. A further, much slower decrease of the pressure can be rationalized by the adsorption of CO_2 on the oxidic support. An increase of the pressure can be explained by the desorption of CO_2 from the copper surface. A deeper, quantitative understanding of the back-titration process

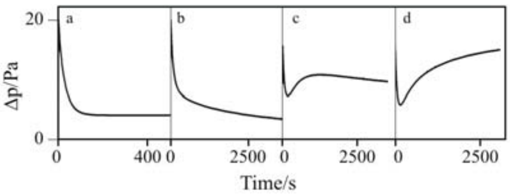

Fig. 4 Change of pressure with time during a dose of adsorptive gas in microcalorimetric experiments: a – theoretical curve for fast and non-activated adsorption without additional processes; b – back-titration of Cu_{75} Al, dose 1 of 21; c – back-titration of $Cu_{75}Al$, dose 6 of 21; d – back-titration of Cu_{75} Al, dose 7 of 21

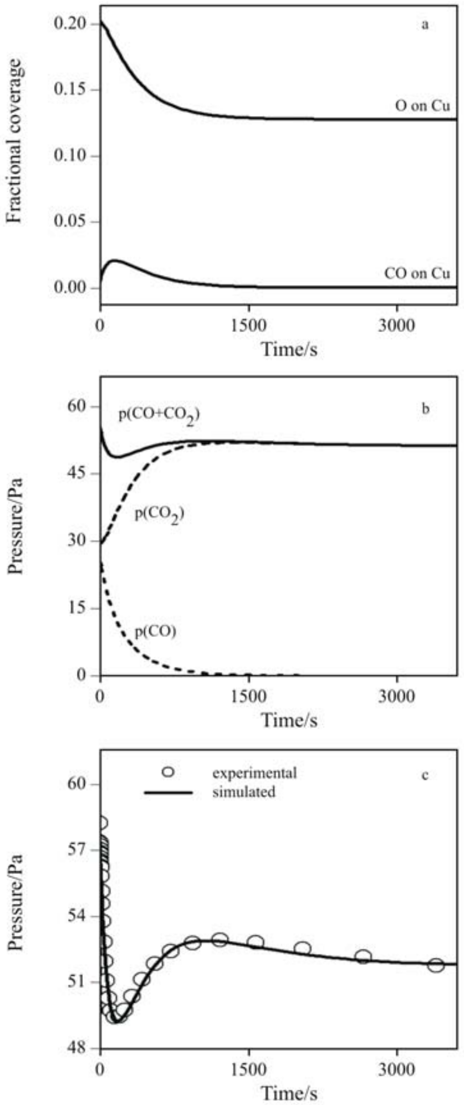

Fig. 5 Results of the kinetic simulation of the sixth dose of the back-titration experiment using $Cu_{75}Al$. a – fractional coverage of adsorbed oxygen and carbon monoxide as a function of time; b – simulation of the partial pressures of CO and CO_2 and the resulting total pressure; c – comparison of experimental and simulated pressure data. The rate constants used in the simulation are: k_{a1}=2.4·10^{-5} $Pa^{-1}s^{-1}$, k_{d1}=2.6·10^{-3} s^{-1}, k_2=3.9·10^{-2} s^{-1}, k_{a4}=4.0·10^{-7} Pa^{-1} s^{-1} and k_{d4}=1.1·10^{-3} s^{-1}

can only be reached by fitting the microkinetic model to the experimental data.

As an example, the results of the simulation of the sixth dose of CO of the back-titration experiment using $Cu_{75}Al$ are shown in Fig. 5. The simulation indicates that CO is completely adsorbed during the dose, and that adsorbed CO is completely consumed by the surface reaction with preadsorbed O, i.e. under equilibrium conditions chemisorbed O and chemisorbed CO do not coexist on a metallic Cu surface. For the simulation of the results shown in Fig. 5, k_2 (Eq. (2)) is set to 0.04 s^{-1}. This means the surface reaction occurs fast and is not or only weakly activated. The partial pressure of CO_2 increases quickly with the consumption of adsorbed CO, and decreases slowly due to the adsorption of CO_2 on the support. For the complete duration of the dose, the simulated total pressure is in very good agreement with the experimental pressure data.

The knowledge derived from the microcalorimetric simulation can be used for the processing of the microcalorimetric raw data obtained during the back-titration. Figure 6 shows the resulting profiles of the differential heat and the adsorption isotherm for the back-titration experiment using $Cu_{75}Al$. The results show clearly that the back-titration is finished after an amount of CO of about 80 μmol g_{cat}^{-1} is adsorbed. In this range, heats of adsorption of about 120–70 kJ mol^{-1} are measured, and the partial pressure of CO is zero when equilibrium is reached. The heat of adsorption is in good agreement with the heat of adsorption of CO on partially oxidized Cu catalysts given in [24] (110–70 kJ mol^{-1}). The influence of strongly reducing conditions on the adsorption of CO on Cu catalysts, including $Cu_{75}Al$, was studied by Naumann d'Alnoncourt *et al.* [14]. The results of the present study in the coverage region above 80 μmol/g^{-1}_{cat} cat are in good agreement with the heat of adsorption and the adsorption isotherm presented

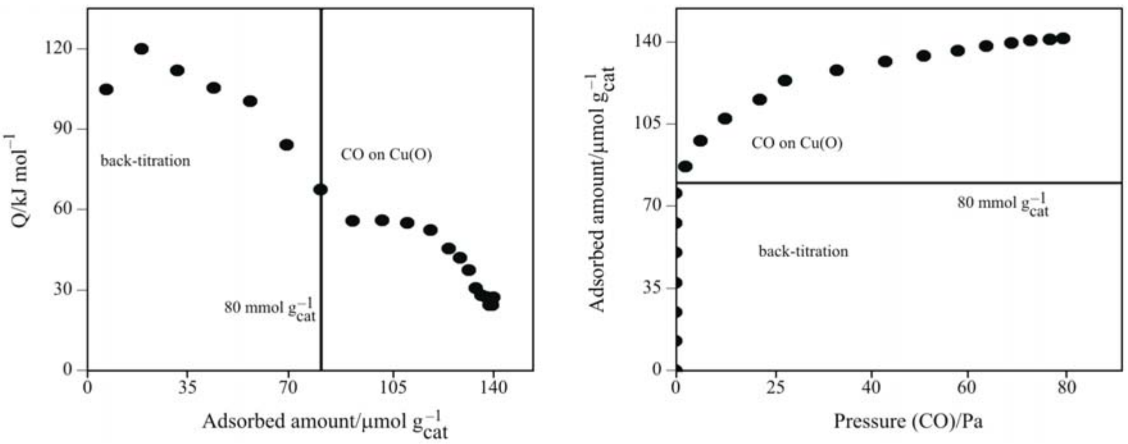

Fig. 6 Results obtained with $Cu_{75}Al$ for the differential heat and the adsorption isotherm of CO on Cu with preadsorbed oxygen taking the results of the microkinetic modelling into account. The back-titration can be clearly distinguished from the adsorption of CO on the metallic Cu present after the back-titration

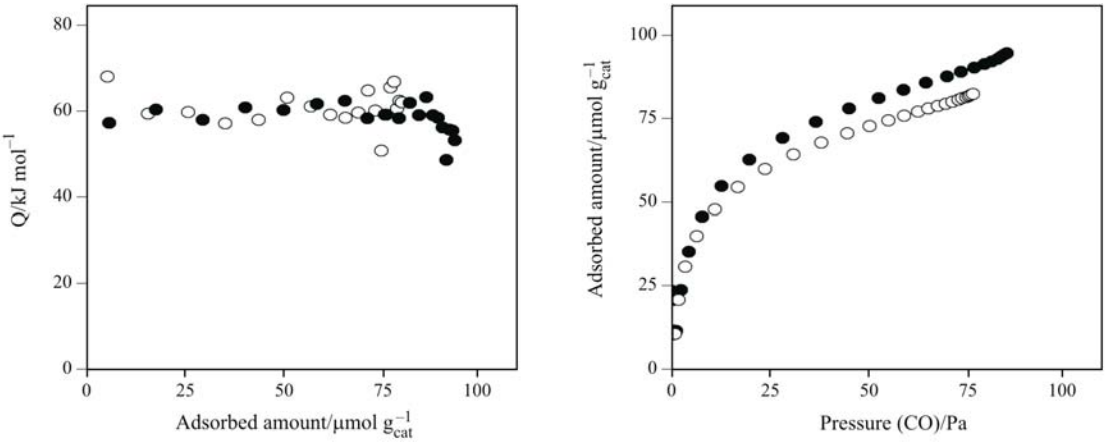

Fig. 7 Results obtained for the differential heat of adsorption of CO on $Cu_{50}ZnAl$ prior to the surface oxidation by N_2O (filled symbols) and after the back-titration using CO (hollow symbols). The experiments are carried out to probe the full reversibility of the surface oxidation via back-titration using CO. The slight decrease of the sorption capacity of the sample can be rationalized by sintering during oxidation and back-titration

in [14], when shifted by a value of 80 μmol g_{cat}^{-1}. This agreement indicates that Cu is completely reduced to its zero-valent state after the back-titration and that the metallic Cu surface is totally free of chemisorbed O. The amount of 80 μmol g_{cat}^{-1} of CO required for the back-titration of chemisorbed O is in reasonable agreement with the value of 88 μmol g_{cat}^{-1} of chemisorbed oxygen measured by N_2O RFC for the formation of a complete monolayer of Cu_2O.

Further evidence for the complete reversibility of the surface oxidation of Cu by N_2O via back-titration of the chemisorbed O using CO is given in Fig. 7. The heat of adsorption and the adsorption isotherm of CO on $Cu_{50}ZnAl$ measured first prior to N_2O adsorption and then after the back-titration are in very good agreement, thus indicating that the state of the Cu surface is identical before oxidation and after reduction.

Conclusions

The amount of oxygen adsorbed on the Cu surface during static N_2O adsorption carried out in the microcalorimetric set-up and during N_2O RFC carried out in a conventional flow set-up are in very good agreement.

The heat of adsorption of N_2O on Cu is constant and independent of coverage. However, not all admitted N_2O reacts with the Cu surface. The residual pressure of N_2O increases as the coverage increases. Bulk oxidation occurs only to a low degree.

The surface oxidation by N_2O can be completely reversed by back-titration with CO. A microkinetic model for the back-titration is presented. The surface reaction of adsorbed CO and preadsorbed O is fast and not or only weakly activated. In equilibrium, chemisorbed CO and chemisorbed O cannot coexist on the Cu surface. The formed CO_2 desorbs instantaneously from the Cu surface and is partially adsorbed on the oxidic support.

After the back-titration, Cu is again completely reduced to its zero-valent state, and the Cu surface area is totally free of chemisorbed oxygen atoms.

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