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Temperature-programmed desorption of H_2 as a tool to determine metal surface areas of Cu catalysts

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Temperature-programmed desorption of H_2 (H_2 TPD) is shown to be a useful new tool for the determination of Cu metal surface areas. The technique has been employed in on-line characterization of binary Cu/Al_2O_3 and ternary $Cu/ZnO/Al_2O_3$ catalysts in a combined TPD–microreactor setup. The catalysts were studied both after reduction and after water gas shift activity tests. A main H_2 TPD peak is observed around 300 K which can be assigned to desorption from Cu metal surface sites. The H_2 TPD method is compared with the N_2O frontal chromatography method which has been extensively used in previous studies for the determination of Cu surface areas. It is found that the dissociative adsorption of N_2O may induce significant changes in the catalyst structure leading to errors in the surface area determination. With the H_2 TPD procedure such irreversible changes can be avoided. A further advantage of the H_2 TPD method is the possibility of providing insight into the nature of the exposed Cu metal surfaces.

Keywords: H_2 temperature-programmed desorption; surface area determination; copper catalyst; N_2O frontal chromatography

1. Introduction

Cu catalysts find widespread use for the water gas shift reaction and for the synthesis of methanol [1,2]. The search for reliable methods for determinations of Cu surface areas has been the subject of many investigations. Several methods have been proposed and in recent years the most frequently advocated method has been the dissociative adsorption of N_2O [3]. The basis of this method is the possibility to achieve half a monolayer of adsorbed atomic oxygen on single crystal surfaces of copper [4]. However, in the case of real catalysts, several complications may arise. For example, it may be difficult to reach the

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coverage of half a monolayer without also having some oxidation of the bulk. In addition, other components in the catalysts may dissociate N_2O. These complications of course render the resulting Cu surface areas somewhat uncertain. To minimize the above problems, many studies have dealt with optimizing the experimental conditions for the N_2O method [5–10] and most researchers have adopted the frontal chromatography approach [7–9].

In view of the above mentioned difficulties, we have investigated alternative means for obtaining Cu particle size and surface area information. These efforts have included the use of in situ EXAFS [11,12] and in situ XRD [13] and recently also temperature-programmed desorption (TPD) of hydrogen (a preliminary account of the method was given by the authors in ref. [14]). The objective of the present report is to discuss the main features of the latter technique and it will be shown that the method can be used to reliably determine the number of exposed Cu metal atoms.

Adsorption and desorption of H_2 have been studied on Cu catalysts [15–17] and have also received considerable interest in surface physics [18–21] since it is one of the main examples of activated adsorption. This feature is an advantage in the present TPD experiments since one can avoid the added complications of readsorption which often give rise to substantially broadened and shifted TPD peaks. Besides providing information about the Cu surface areas, the H_2 TPD method may also provide insight into the nature of the exposed Cu surfaces. A few publications have previously dealt with hydrogen desorption from Cu catalysts [15–17]. However, to our knowledge this is the first report on using the technique in a quantitative manner employing an on-line TPD–microreactor system.

2. Experimental

The essential features of the experimental setup will be described below and further details will be discussed elsewhere [22]. All experiments were carried out in a computer-controlled, all stainless steel, TPD–microreactor system which could be operated at pressures up to 100 bar. The gases used had the following purities: He 99.9999%, H_2 99.9997%, CO 99.997%, CO_2 99.998%, N_2O 99.998%. CO, CO_2 and H_2 used for the water gas shift (WGS) reaction were further purified after mixing by means of a guard reactor filled with sulfur and chlorine absorbers (Haldor Topsøe LSK and LK-801 commercial systems). The flows were controlled by electronic mass flowmeters and the temperatures by microprocessor controllers. Steam was added to the feed by vaporizing ion exchanged and degassed water whose flow was controlled by a liquid mass flowmeter. The reactor consisted of a glass lined U-tube similar to the one described in ref. [23]. The empty reactor was found not to give any desorption of H_2 within the limits of detection. The U-tube was placed in an aluminum cylinder which could be heated to 800 K or cooled to 78 K by means of liquid nitrogen. All parts of the system in contact with water vapor were heated to avoid condensation. Gas analysis was performed by a mass spectrometer (Balzers GAM 445) which was calibrated by using reference gas mixtures. In all TPD experiments reported here the heating rate was 6 K/min.

Two types of Cu catalysts were used in the experiments. One of these was a binary Cu/Al_2O_3 catalyst prepared by coprecipitation of nitrates according to the procedure given in ref. [24] (wt% Cu = 35; BET surface area = 150 m^2/g; pore volume = 0.4 cc/g; all data are on a fresh catalyst basis). The other was a commercial ternary $Cu/ZnO/Al_2O_3$ water gas shift catalyst (Haldor Topsøe LK-821: wt% Cu = 40; wt% Zn = 21; BET surface area = 75 m^2/g; pore volume = 0.4 cc/g; all data are on a fresh catalyst basis). Usually 260 mg of a 0.150–0.300 mm sieve fraction was used resulting in a bed height of about 25 mm. The absence of any diffusional limitations was verified by carrying out Ar effusion experiments [22].

The reduction of the catalysts was carried out in a mixture of 0.5% CO, 4% CO_2 and 4% H_2 in Ar with a heating ramp of 0.6 K/min. The final reduction temperature was 493 and 513 K for the ternary and binary catalysts, respectively. The catalytic WGS activity was determined at 493 K far from equilibrium, at atmospheric pressure or 5 bar using an industrial-type feed (1.4% CO, 12.9% CO_2, 52.9% H_2 and 32.8% H_2O).

The N_2O experiments were carried out in the microreactor–TPD system by switching from 30 Nml/min He to 30 Nml/min of 1% N_2O in He at 333 K The total amount of N_2 formed was calculated by integrating the N_2 concentration from the onset of N_2 formation to the extrapolated cut-off according to the procedures given in ref. [7].

3. Results

Fig. 1 displays hydrogen TPD traces for the two catalysts obtained after different TPD and activity test conditions. The most pronounced feature of the spectra is a symmetric peak around 300 K the area of which is given in table 1. The areas could be reproduced within 5% and were obtained by integration after subtraction of a linear background drawn through the minima at each side of the peak. In view of the activated nature of hydrogen adsorption on Cu, different experimental conditions for the hydrogen dosage were examined in order to find an adequate procedure for achieving a reproducible coverage. Traces A and B of fig. 1 show the hydrogen TPD experiments for the binary Cu/Al_2O_3 catalyst. In each case, a freshly reduced catalyst was used. In trace A, the reduction was followed by flushing in H_2 (100 Nml/min) at 493 K and subsequent cooling in hydrogen to about 250 K (i.e. below the desorption temperature). The catalyst was kept at this temperature (= holding tempera-

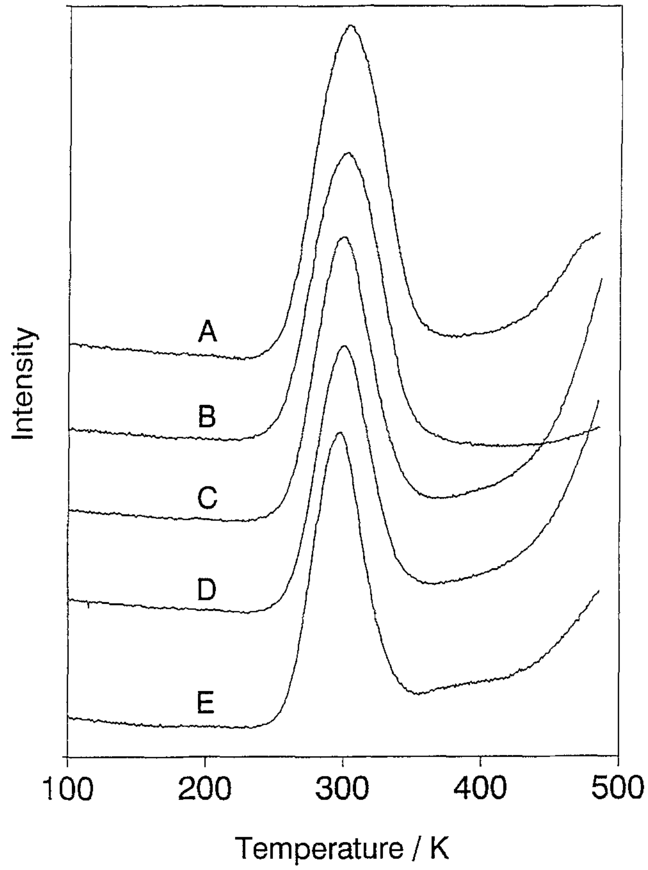

Fig. 1. (A) H_2 TPD spectrum from On/Al_2O_3 after reduction, switching to pure H_2 at 493 K, flushing and subsequent cooling in H_2 to 250 K, holding this temperature for 60 min and finally cooling to 78 K. (B) Similar to A except that the sample was cooled in pure He from 493 to 300 K after reduction. At this temperature the gas was switched to pure H_2 and the sample cooled to 250 K, kept at this temperature for 60 min and subsequently cooled to 78 K. (C) Spectrum from Cu/ZnO/Al_2O_3 with pretreatment as A. (D) As C except that the holding time at 250 K was omitted, i.e. cooling directly from 493 to 78 K in pure H_2. (E) As C except that the H_2 adsorption was carried out after 60 h of water gas shift reaction at 5 bar.

ture) for about 60 min (holding time) and then cooled to 78 K. The gas was changed from hydrogen to helium (also 100 Nml/min) and flushed for 40 min before carrying out the TPD. Trace B is a similar TPD spectrum with the only difference being that the sample was cooled from reduction temperature to 300 K in He before the exposure to hydrogen was carried out. As can be seen both from fig. 1 and table 1, the area is about 10% smaller with no significant change in the peak position.

Traces C, D and E of fig. 1 are the hydrogen TPD spectra for the ternary catalyst samples. The pretreatment corresponding to C is the same as the pretreatment corresponding to A. In the experiment of trace D, the 60 min H_2

Table 1

Catalyst	μmol H_2/g cat. from H_2 TPD	μmol N_2/g cat. from N_2O	Comments
Cu/Al_2O_3	96	–	a
	87	112	b
	58	107	c
	92	–	d
	96	–	e
	23	46	f
$Cu/ZnO/Al_2O_3$	66	–	g
	60	–	h
	59	–	i

[a] See trace A in fig. 1.

[b] First the H_2 TPD was carried out (trace B in fig. 1) and immediately thereafter the N_2O frontal chromatography.

[c] The H_2 TPD just after the N_2O experiment of b and subsequently a new N_2O experiment.

[d] Freshly reduced.

[e] Immediately after d to check the reproducibility.

[f] After carrying out WGS at 5 bar for 20 h; first the H_2 TPD then the N_2O experiment.

[g] Trace C in fig. 1.

[h] Trace D in fig. 1.

[i] Trace E in fig. 1.

exposure time at 250 K was omitted resulting in a 10% decrease in the amount of H_2 desorbed. Trace E is a hydrogen TPD spectrum recorded after carrying out water gas shift at 5 bar for 60 h. No large change in the area of the peak at 300 K is observed but a new peak at about 390 K is noted. As discussed in ref. [16], this peak is probably due to hydrogen desorption from copper oxide species.

In order to test whether the H_2 TPD measurements may cause irreversible changes in the catalyst structure, repeated sequences of H_2 TPD measurements have been performed. The results (Table 1) showed no differences in the H_2 TPD peak areas or shapes.

In fig. 2, the amount of N_2 formed from the dissociative adsorption of N_2O is plotted against the area of the H_2 TPD peak recorded immediately before the N_2O experiments.

4. Discussion

For both binary Cu/Al_2O_3 and ternary $Cu/ZnO/Al_2O_3$ catalysts, a pronounced hydrogen TPD peak is observed around 300 K. In view of the previous catalyst studies by Roberts and Griffin [16] and Pan et al. [17], and the single crystal studies of Anger et al. [18], this peak can unequivocally be assigned to

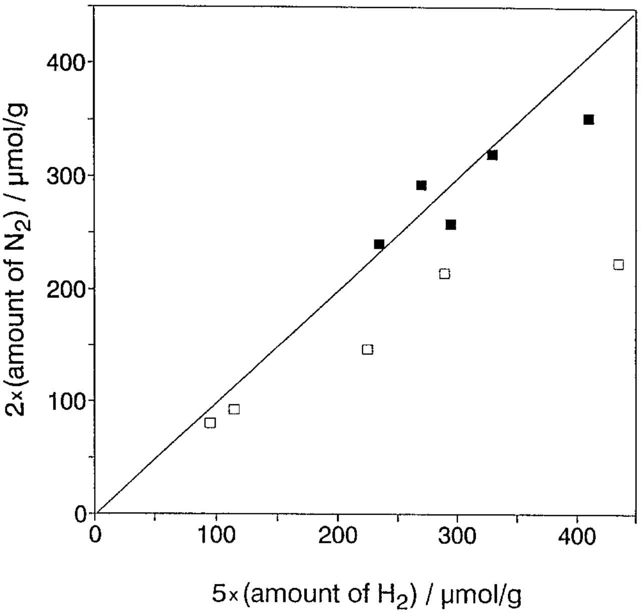

Fig. 2. The amount of copper as measured by the N_2O frontal chromatography method versus the amount obtained from the H_2 TPD method, in µmol copper per gram catalyst. Since the H_2 molecule probes two copper sites, the value from the H_2 TPD must be multiplied by two, and further by 2.5 assuming a hydrogen coverage of 0.4. The value from the N_2O method has to be multiplied by two in order to obtain the amount of copper since the saturation coverage for oxygen is 0.5. The filled and open squares are for $Cu/ZnO/Al_2O_3$ and Cu/Al_2O_3, respectively.

desorption from Cu metal surface sites. This peak is clearly separated from desorption features which in some cases may occur at higher temperatures. The origin of the latter species will be discussed in ref. [22]. In order to calculate the number of exposed Cu surface atoms from the TPD peak areas, it is necessary to know the hydrogen coverage. In this connection, it is advantageous that the same saturation coverage of hydrogen (corresponding to H/Cu = 1/2) has been observed on all three low-index planes of Cu [18]. Since the adsorbed hydrogen and the hydrogen in the gas phase are in equilibrium at higher temperatures and approaching equilibrium at lower temperatures, the choice of adsorption procedure (cooling rate, holding temperature, holding time, etc.) influences the obtained coverage. From the existing data on the adsorption/desorption constants for the H_2/Cu system [18,25,26], we calculate a coverage in the range 0.35–0.45 under our conditions. (This will be discussed in greater detail in ref. [22].) Also, a coverage of 0.4 results in Cu surface areas which fit well with areas obtained by N_2O frontal chromatography for samples where the latter technique gives reliable results (see below).

It should be pointed out that high temperature exposure to pure hydrogen may lead to significant changes in the sample. This phenomenon was observed to be dependent on the type of samples and was pronounced for the ZnO containing ternary catalysts [22]. Also, high temperature exposure to hydrogen has recently been observed by van der Grift et al. [27] to change the structure of Cu/SiO_2. The above changes in the samples can be avoided by performing the hydrogen exposure at 300 K.

It is found that adsorbed oxygen species on the metallic Cu surface are removed by hydrogen exposure even at 300 K, whereas higher exposure temperatures are needed to reduce any bulk-like copper oxide that might have formed, e.g., during synthesis conditions. Since the objective here is to use the H_2 TPD method to measure only the number of exposed Cu metal surface sites present at certain reaction conditions, it is recommended that the H_2 exposure is carried out at room temperature and below.

In the present study, the N_2O frontal chromatography method was employed in order to compare the results of this method with the hydrogen TPD. For the freshly reduced Cu/Al_2O_3 catalyst, the interaction of N_2O was found to cause significant changes in the catalysts since the amount of H_2 desorbed after the N_2O experiment was 33% less than before. The decrease in number of Cu sites could be due to some sintering caused by the high amount of heat released during the N_2O dissociation. Indeed, such a sintering process is much more likely to be induced by N_2O decomposition than by hydrogen adsorption since the heat of the dissociative adsorption of N_2O is much larger than the heat of hydrogen adsorption. The changes caused by the N_2O decomposition will depend on the ability to accommodate the heat being released and are therefore expected to be especially large for samples containing small particles with a large ratio of surface to bulk atoms. In agreement with the above, the N_2O method appeared to give more reproducible values of the surface areas for aged samples. For example, after 20 h of water gas shift reaction at 5 bar, good agreement between the hydrogen TPD and the N_2O method was obtained (table 1 and fig. 2). Besides the possibility of bulk oxidation, other reactions may also influence the N_2O adsorption as will be discussed elsewhere [22]. Nevertheless, for the present purpose it is clear that the N_2O method may be subject to severe complications which makes it less attractive compared to the present H_2 TPD method.

In order to estimate surface areas from the determination of the number of exposed surface atoms, it is necessary to have information about the type of surface planes exposed. Usually, such information is not available and one makes assumptions on the density of surface atoms (for example, using the values for the most stable surface planes or an average of the densities of the low-index planes). This has also been the case in the previous studies employing, e.g., the N_2O chemisorption method. Regarding the type of surface planes exposed, it is interesting to note that a recent microkinetic analysis of the water gas shift reaction [28] points to the presence of Cu(111) planes. We have attempted to obtain some insight into the nature of the exposed surface planes by modelling the hydrogen TPD spectra using available single crystal data [18] for the desorption kinetics. The results from the modelling do not unambiguously point to one particular low-index plane as constituting the surface of the copper particles. It was not possible to carry out simulations of the desorption from Cu(100) since the single crystal data are quite complex and possibly involve the lifting of a surface reconstruction [18]. However, the peak position would come out much too low in comparison to the experiments. For Cu(111), the peak maximum is around 275 K, i.e. about 25 K too low but the width is similar to the experimental one. Finally, the peak position of the modelled desorption from Cu(110) coincides with the experimental value, while the width is only one third of the measured one. It is known that defects, such as steps, can increase the binding energy of the order 10 kJ/mol (see, e.g., the report on Pd(111) [29] and Pt(111) [30]) and by taking this into account, the modelled desorption peak from Cu(111) can be moved to coincide with the experimental one. The possible presence of steps and higher order planes will be addressed in ref. [22] together with a more detailed description of the modelling.

5. Conclusion

The temperature-programmed desorption of H_2 has been shown to be a reliable tool to determine Cu metal areas. In order to avoid the reduction of any bulk oxide it is recommended to lower the temperature to 300 K before exposing the sample to H_2, and in order to obtain reproducible hydrogen coverages it is further recommended to keep the sample temperature around 250 K for one to two hours before cooling the sample to liquid nitrogen temperature. It is seen that the H_2 TPD method does not have some of the drawbacks that may be encountered with the N_2O frontal chromatography method, e.g., modification of the Cu particle structure which, most likely, is caused by the large heat of dissociative adsorption of N_2O. The copper surface areas obtained by H_2 TPD agree well with those of the N_2O method for samples where the N_2O method gives reliable results.

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