MEASUREMENT OF SPECIFIC COPPER SURFACE AREA BY A PULSE CHROMATOGRAPHIC TECHNIQUE

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The method for determination of specific copper area by decompositive adsorption of N_2O has been investigated using pulse chromatographic technique. The reaction is accompanied by activated adsorption of oxygen. The amount of oxygen adsorbed depends linearly upon the temperature in the range of -20 to $+90°C$. The existence of an oxygen monolayer in the temperature range from 90 to 120°C has been proved. On the surface, the Cu : O ratio is equal to 2. The rate of decompositive N_2O adsorption is very high. The weakly bonded oxygen can be desorbed at 100°C into a stream of inert gas and the rate of oxygen desorption depends on the temperature of decompositive N_2O adsorption. An improved procedure for measuring copper surface area by pulse chromatographic technique have been suggested.

Most frequently, metal surface areas are determined by chemisorption of a suitable sorbate. From the results summarized by Scholten[1,2], it follows unambiguously that N_2O is the best adsorbate for selective chemisorption on copper surfaces. Other adsorbates, such as H_2, CO and O_2, have been largely unsuccessful as their ready chemisorption is accompanied either by physisorption or by a slow bulk oxidation. However, a successful low-temperature oxygen chemisorption procedure has been described by Parris and Klier[3] recently.

The reaction of nitrous oxide with copper surfaces was first studied by Dell, Stone and Tilley[4], and the use of decompositive N_2O adsorption for determining the copper surface area of supported catalyst was first recommended by Osinga and coworkers[5]. Since then, many investigators[6–12] used N_2O chemisorption to evaluate metal surface areas of both pure and supported copper catalysts. This technique is based on the decomposition of N_2O molecules by contact with surface copper atoms to give rise to chemisorbed oxygen atoms and gaseous nitrogen according to reaction (*A*).

$$N_2O(g) + 2\,Cu(surf) \rightleftarrows N_2(g) + (Cu\text{—}O\text{—}Cu)\,(surf) \quad \Delta H = -167{\cdot}5\ \text{kJ mol}^{-1} \quad (A)$$
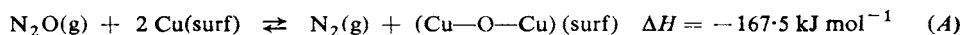
Previously the amount of chemisorbed oxygen was usually determined by two indirect methods. The first one was based on the measured heat of N_2O chemisorption and, as a complement to the uptake of oxygen, was used by both Dell et al.[4] and Giamello et al.[6] More frequently the amount of liberated N_2 was applied to the same purpose but the detection method was different. Some authors[4,5,7,8] monitored the amount of evolved nitrogen in a static system by freezing out excess N_2O and determining the residual pressure in a volumetric apparatus.

Scholten and Konvalinka[3] used a TC-detector and a mass spectrometer to analyse the nitrogen in a gas mixture circulating above the catalyst. The TC-detector was also used by Dvořák and Pašek[9], Evans et al.[10] and Chinchen and coworkers[11] to determine the nitrogen concentration in a stream of gas mixture passed over a catalyst sample.

The results of the cited investigators disagree. This is caused both by different definitions of the parameters used in evaluating the data (Table I) and by discrepancies in experimental results (Table II). Differences in definitions of parameters has already been exhaustively and critically discussed by Evans and coworkers[10]. To characterize the copper sites for oxygen uptake via reaction (*A*) they used an average value of the surface atom density. The value of this parameter depends on the surface distribution of (100), (110) and (111) crystallographic planes. Evans and coworkers[10] have assumed and recommended uniform distribution of these planes giving surface concentration of Cu atom $1.46 . 10^{19}$ per m^2. This agrees with the value calculated by Dell et al.[4] using the same assumption but differs from the values of $1.35 . 10^{19}$ reported by Osinga et al.[5], Dvořák et al.[9] and $1.40 . 10^{19}$ calculated in the present work. The value $1.46 . 10^{19}$ atoms m^{-2} was obtained as the average value of the surface atom densities of the (100), (110) and (111) planes reported by Roberts and

TABLE I

Parameters used in the determination of specific copper area

Reference	Characteristic of the copper site		Surface stoichiometry Cu_{surf}/O_{ads}	Surface coverage		
	$\langle A_{Cu}\rangle$ $10^{20} m^2$	$\langle D_{Cu}\rangle$ 10^{-19} atoms m^{-2}		Θ_1	Θ_2	Θ_{ch}
4	6·8	1·47	1	0·2—0·25	—	0·4—0·5
5	7·41	1·35	1	0·35	—	0·7
1	5·88	1·70	2	—	1	1
9	7·41	1·35	1	0·35	—	0·7
10	—	1·46	2	—	1	1
12	—	—	2	—	—	—
7	—	1·78	2	—	—	1
6	—	1·1[a]	2	—	0·6	0·6
8	—	1·70	3·3[d]	—	—	~1[d]
11	—	1·0[b]	2	—	1	1
Present work	7·144	1·40[c]	2	—	—	1

[a] Calculated from uptake O_{ads} on basis of $Cu_{surf}/O = 2$ and $\Theta_2 = 0.6$. [b] Calculated from value of saturated oxygen uptake on basis of $Cu_{surf}/O = 2$. [c] Calculated from average surface area of the copper site. [d] Referred to Chen and Yeh[21].

TABLE II

Comparison of both experimental conditions and results given by various authors

Reference	Experimental conditions		Oxygen uptake/m^2 Cu		Rate of the reaction (A)	Experimental technique	Onset of bulk oxida- tion, °C	Temperature dependence of adsorbed amount
	temperature range, °C	N$_2$O pres- sure, kPa	atoms 10^{-19}	ml O (NTP)				
4	—	0·053	0·295 at 20°C	0·11	—	calorimetry	—	—
5	20—150	80	0·47 from 20 to 120°C	0·176	slow	volumetric static apparatus	<120	A = const. for $t \in \langle 20, 120 \rangle$
1	20—140	26·67	0·85 at 90°C	0·318	very slow	circulate app. with TCD, MSD	~120	$A = f(t_{ads})$ $t \in \langle 20, 100 \rangle$
9	20—100	—	0·47 from 20 to 60°C	0·176	very rapid	pulse chromato- graphy	—	A = const. for $t \in \langle 20, 60 \rangle$
10	25—160	—	0·73 at 90°C	0·271	very rapid	pulse chromato- graphy	~130	$A = f(t_{ads})$ $t \in \langle 20, 120 \rangle$

12	20—150	—	0.14^a at 20°C	0.052^a	very slow	UPS spectrometry	100	$A =$ const. for $t \in \langle 70, 100 \rangle$
7	20—120	26·67	0·89 from 20 to 70°C	0·333	very slow	volumetric static apparatus	∼70	$A =$ const. for $t \in \langle 20, 70 \rangle$
6	20—100	—	0·340 from 20 to 80°C	0·126	slow	microcalorimetry	>80	$A =$ const. for $t \in \langle 20, 80 \rangle$
8	20	101·3	0·51 at 20°C	0·193	rapid	conventional volumetric app.	∼20	—
11	25—90	7·07—36·4	0·5 from 25 to 90°C	0·187	very rapid	reactive frontal chromatography	—	$A =$ const. for $t \in \langle 20, 90 \rangle$
Present work	(−20)—135	—	0·7 from 90 to 125°C	0·262	very rapid	pulse chromatography	>125	$A = f(t_{ads})$ $t \in \langle 20, 125 \rangle$

^{a} Value related to 1 g Cu.

McKee[13]. However, if an average surface area of the copper site is used, an average density of $1 \cdot 40 \cdot 10^{19}$ atoms m^{-2} is obtained. Scholten et al.[1] referring to the experimental work by Sundquist[14] proposed a special crystal plane distribution. Sengupta et al.[7] and Chen et al.[8] have employed the same distribution giving a value of $1 \cdot 70 \cdot 10^{19}$ atoms m^{-2}, identical with Scholten's value. This distribution was established at equilibrium conditions and is therefore energetically the most advantageous and consequently the most probable one. In the practical catalysts, however, the finely divided metal particles are bonded to a support, and sometimes a dispersion stabilizer is added. The metal crystal phase is rich in structural defects and is prepared under conditions which are far from equilibrium. Thus, the use of the equilibrium distribution is not fully justified. The experimental determination of the real distribution of crystal planes is not possible and so the use of uniform distribution may be recommended. The surface coverage is usually defined as the ratio between the occupied and total surface area, regardless of the surface stoichiometry. A similar definition, i.e. oxygen atoms adsorbed per surface copper atoms, has been used by Osinga et al.[5] and Chen et al.[8] .The LEED results by Ertl[15,16] and recently elipsometry and AES studies by Habraken et al.[17] confirmed that the decompositive N_2O adsorption on copper surfaces leads to the formation of species with a structure corresponding to Cu_2O. In the light of these results and in accordance with the amount of oxygen adsorbed on copper surfaces at $\Theta_2 = 1$, the surface stoichiometry $Cu_{surf}/O_{ads} = 2$ adopted by Scholten and Konvalinka[1] and accepted by further investigators[2,6,7,11] is correct. For avoiding confusion, we suggest to define the surface coverage Θ_{ch} for oxygen uptake via decompositive N_2O adsorption as the number of oxygen atoms adsorbed per pair of copper atoms $(Cu \cdots Cu)$ (surf).

The principal differences in the published results[1,5,6,7,10,11] are observed in the temperature dependence of the extent of adsorption and in the value of the oxygen uptake at saturation coverage (Table III). The rate of reaction (A) and the effect of temperature on the extent of bulk oxidation are further discrepancies which are also summarized in Table II.

In contrary to some authors[5,6,7,11] who did not find substantial change in the oxygen uptake by copper with temperature, Scholten and Konvalinka[1] and Evans et al.[10] have observed temperature dependence of it. Evans and coworkers[10] found in the range 25 to 90°C, an increase of adsorbed oxygen by 26%. In the same temperature interval, Scholten and Konvalinka[1] observed almost doubling of oxygen uptake in N_2O decomposition on copper powder. The amount of N_2O necessary to cover 1 m^2 of copper surface with oxygen atoms is reported by different investigators from 0·176 ml (STP) to 0·333 ml (STP).

The rate of reaction (A) is further conflicting parameter. Except the study by Scholten and Konvalinka[1] and the papers using the clasical static technique[5,7,8], all other investigators observed very high rate of N_2O reaction with the copper surface. It is probable, that the Scholten's[1] measurements were performed under

condition of diffusional retardation. The majority of authors reported that approximately 120°C is the onset temperature of bulk oxidation. Similar course in temperature dependence of oxygen uptake has observed by Dvořák and Pašek[9] but in contrast to latter papers[6,7] they did not ascribe it to the onset of copper bulk oxidation.

In the present paper, the conditions for the decompositive adsorption of N_2O by pulse chromatographic technique have been studied in detail in order to elucidate

TABLE III
Reduction conditions and the BET surface area of the copper samples

Sample		Origin	Conditions of reduction				Surface area (BET) $m^2 g^{-1}$
			temperature °C	time and partial pressure of H_2		flow-rate of reductive gas $1 h^{-1}$	
				h	kPa		
I	1	copper powder	220	1·0 at	10·1 and	10·0	3·99
	2	prepared by re-		1·0 at	20·2 and		4·59
	3	duction of CuO[a]		2·0 at	101·1		4·65
II	1	the same as I	220	1·0 at	10·1 and	10·0	1·77
	2	but sintered		1·0 at	20·2 and		2·01
	3			2·0 at	101·1		2·40
III	1	copper powder	200	3·0 at	10·1 and	6·0	4·21
	2	prepared by re-		1·5 at	20·2 and	.	4·83
	3	duction of CuO[a]		1·0 at	101·1		4·97
IV	1	copper powder	200	3·0 at	10·1 and	6·0	4·66
	2	prepared by re-		1·5 at	20·2 and		5·02
	3	duction of CuO[a]		1·0 at	101·1		5·23
V	1	reduction of the	220	2·0 at	10·1 and	10·0	see
	2	commercial		1·0 at	20·2 and		
	3	catalysts		3·0 at	101·1		Table V

[a] Prepared by calcination of $Cu_2(OH)_2CO_3$ (from Lachema Brno) in air at 300°C for 8 h; $S(BET) = 23 \, m^2 \, g^{-1}$.

the discrepancies in the literature. Attention was also given to the cause of the so
called rest-peak observed earlier by Dvořák and Pašek[9] and Evans et al.[10]. As the
result a standard procedure for determining specific copper surface area is recom-
mended.

EXPERIMENTAL

The apparatus was in principle the same as described in our preceding paper[9]. Higher purity
of the carrier gas was achieved; its oxygen content was lower than 1 ppm. The sensitivity of
a four-filament katharometer was better than of the two-filament type used previously. A pneu-
matically controlled six-way sampling walve was applied which enabled further improvement
of the procedure. A chromatographic separation of N_2 and excess N_2O was carried out on
styrene–divinylbenzene–acrylonitrile copolymer at $-20°C$ which allowed to inject twelve pulses
before the peak of N_2O appeared. The detailed scheme and description of the innovated apparatus
has been published by Dvořák and Hudec[18].

Catalyst. The pure copper powders and supported copper catalysts were prepared by hydrogen
reduction of CuO and copper precursors, respectively, under the conditions given in Table III.
Each group of samples (I—V) was reduced at special conditions. Individual samples (1—3) in
these groups were prepared at practically identical reduction conditions. The samples were
placed in glass tube of 4 mm i.d. and heated in a bath with a low-melting alloy[19]. In order to
suppress the effect of water on reduction, the reduction of the individual samples in a group was
started after 1/2 hour interval. The reactivation of samples exposed to N_2O was carried out in
the stream of purified hydrogen during 0·5 h at 220 and 200°C, respectively. Hydrogen from pres-
sure bottles was purified over a reduced copper catalyst (BASF, R 3—11), and dried over mole-
cular sieve NALSIT 4A. The last traces of water were frozen out at 77 K. Three types of sup-
ported catalyst were investigated: 1. Catalyst on a silicate support (ZCH Oswięcim, Poland, types
NA and NA-2T, and BASF, F.R.G., type R 3—11); 2. a low-temperature CO conversion catalyst
(BASF, F.R.G., type K 3—10); 3. copper chromite catalyst both with and without a dispersion

TABLE IV

Standard procedure for determining specific copper surface area by a pulse chromatographic
technique

Parameters	Conditions
Temperature	100°C
Volume of the N_2O-pulse at 0·1 MPa and 20°C	1—3 ml
Frequency of N_2O pulses	$1/40\ s^{-1}$
The wash-out period of the sampling loop	20 s
Minimum sample weight	>1 g
Sample grain size	0·4—0·6 mm
Oxygen content in the carrier gas	<1 ppm
Carrier gas flow-rate	$25—50\ ml\ min^{-1}$
Sample bed	carefully packed in vertical position

stabilizer (Harshaw Chemical Co., U.S.A., types Cu-1107, Cu-1808 and Cu-122/2, and Nikky. Chemical Co., Japan, type N-202 D).

Specific copper surface area determination. Prior to determination of the surface area either by means of the BET method or by the chemisorption technique, each catalyst was reduced (see Table III) or reactivated. At the end of reduction a gas mixture (He + N_2) or pure helium was passed through the catalyst bed for 20 minutes to remove hydrogen from the apparatus.

The three-point procedure was used to determine the BET surface area by the chromatographic flow method, first described by Nelson and Eggertsen[20]. Calibrated gas mixtures containing 8, 18 and 26 vol. % nitrogen in helium were used; the final amount of oxygen in all mixtures used was lower than 1 ppm. Replicate experiments showed that the N_2 surface areas had standard deviations of $\pm 3 \cdot 5\%$.

The pulse-flow method for decompositive adsorption of N_2O was already described else-where[9,18] and the conditions of the new standard procedure are summarized in Table IV. The pulses of N_2O were injected into the stabilized helium stream using a six-way valve, which had interchangeable calibrated and tempered loops (volumes from $0 \cdot 87$ to $8 \cdot 23$ cm^3). Two procedures for N_2O injection were used. In the first one (cf.[9]), the individual pulses of N_2O were introduced after the separation of the N_2–N_2O mixture from the previous pulse was finished (see Fig. 1); a column 1 m × 0·4 cm containing ADS copolymer at approximately 22°C was applied for the separation. For the new standard procedure different way for introducing the samples is recommended. The column temperature of -20°C allowed to inject 10 to 12 consecutive N_2O pulses in 40 s intervals until the first peak of N_2O appeared (Fig. 2). The amount of N_2 evolved was equal to the N_2O decomposed by reaction (A) and was determined by absolute nitrogen calibration. For the specific surface area determination, the sum of N_2 peak areas was used, after the rest-peak area has been substracted from all N_2 peaks except the first one.

Desorption experiments. The same apparatus and technique was used to study the decompositive adsorption of N_2O on restorated copper surfaces obtained by passing the carrier gas at 100°C over the catalyst, previously covered by oxygen from decomposition of N_2O. The purpose was to get indirect evidence on the desorption of weakly bonded O_{ads} from fully occupied copper surface. An attempt to obtain direct evidence was not conclusive; no oxygen was found in getter (77 K) collecting gases desorbed during $0 \cdot 5$ h passing of pure helium over the sample which was before covered by oxygen monolayer.

RESULTS AND DISCUSSION

The technique initially used to the measurement of specific copper surface area was the same as that described in our previous work[9]. The experiments were started with sample groups I and II; they were pure copper powders with different N_2 specific area and their preparation and properties are specified in Table III and an example of the measurements is in Fig. 1. The amount of decomposed N_2O rapidly decreases with increasing surface coverage. However, the decomposition of N_2O doesn't stop completely but it is established at an approximately constant value independent of the number of pulses. The liberated amounts of nitrogen, i.e. the N_2 peaks after fourth and further pulses (Fig. 1) will be called rest-peaks.

From the kinetics investigations by Scholten and Konvalinka[1] it follows that the rate of decompositive N_2O adsorption is relatively slow. Therefore, it might be

assumed that the rest-peak corresponds to that part of adsorbed oxygen covering the residual free fraction of the copper surface. However, comparison of the N_2 specific copper surface area of pure copper powders with the amount of O_{ads} necessary to form a monolayer showed that it is already filled where the first rest-peak appears. This indicated that the rate of reaction (A) is fast enough and it is in accordance with the conception now generally accepted.

Rest-Peak Origin

In order to elucidate the origin of the rest-peak, the following possible causes were considdered: a) Diffusion of free copper atoms from the bulk towards the surface layer already blocked by adsorbed oxygen. b) Reaction of N_2O with adsorbed O_{ads} resulting in the liberation of N_2 and formation of chemisorbed O_2. c) Desorption of weakly bonded O_{ads} leading to partial restoration of the free copper surface.

The effect of reaction conditions on the size of the rest-peak were investigated: the reaction temperature, the amount of N_2O introduced in one pulse, the flow-rate of carrier gas and the frequency of N_2O pulses. The experimental results may be summarized as follows: *1.* The size of the rest-peak increases with increasing temperature in the range of $20-120°C$ (Fig. 3). *2.* The size of rest-peak is independent of the amount of N_2O introduced in one pulse. *3.* The amount of N_2 liberated through the N_2O reaction with restored copper surface increases with the flow-rate of the carrier gas for the restoring used (Fig. 4). *4.* The size of rest-peak depends on the
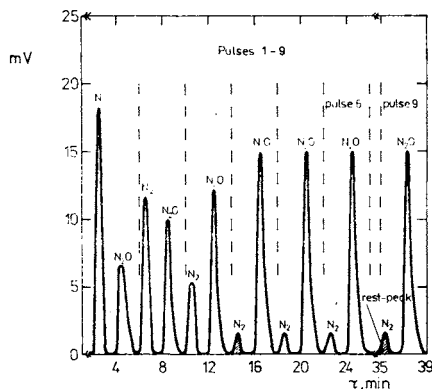

FIG. 1

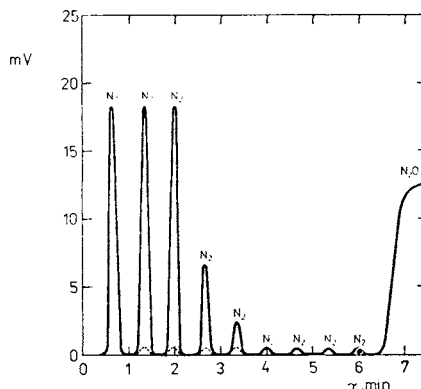Chromatographic record of the decompositive N_2O adsorption on a copper surface (an illustrative example)

FIG. 2

Chromatographic record of the decompositive N_2O adsorption on a copper surface by improved procedure (experimental conditions see Table IV)

frequency of N_2O pulsing. The amount of decomposed N_2O increases with increasing time interval between two pulses. The rest-peak appears in the flow-system only. In the closed system the rest-peak was not observed even after longer intervals (severals hours).

The results summarized in points *2* and *3* neither support nor exclude the explanation of the origin of the rest-peak by a reaction of N_2O with oxygen atoms adsorbed on the surface. However, a course of this reaction cannot be influenced by the frequency of N_2O-pulses (see point *4*). It follows from observations *1* and *2*, partially also from point *4* that the cause of the rest-peak is restoration of a certain fraction of the copper surface for the decompositive N_2O adsorption in the period between two pulses. It may be caused by diffusion of copper atoms from the bulk towards the surface (cause *a*) or by desorption of weakly bonded oxygen species (cause *c*). From these two possibilities, only the desorption of weakly bonded O_{ads} (cause *c*) can explain the dependence of the rate of copper surface restoration on the flow-rate of the carrier gas (observations *3* and *4*).

This indirect evidence of the rest-peak origin is further supported by desorption experiments; their results can be summarized as follows: a) The generation of copper surface area, which was ascribed to the desorption of O_{ads}, is perfectly reproducible. The fraction of desorbed oxygen is independent of the number of repeated adsorption and desorption cycles conducted at the same conditions. However, the amount of
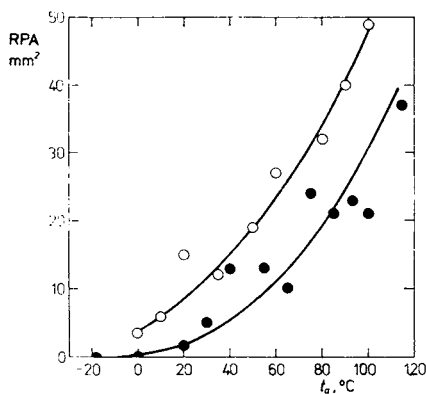

FIG. 3

Dependence of the rest-peak area (RPA) or of the fraction of restorated copper surface on the adsorption temperature t_{ads}. Experimental conditions: $1.7\ l\ h^{-1}$ He, $t_{des} = t_{ads}$, $\bigcirc$ sample I-2, $\bullet$ sample II-1, weight of samples: 1.95 g and 2.01 g
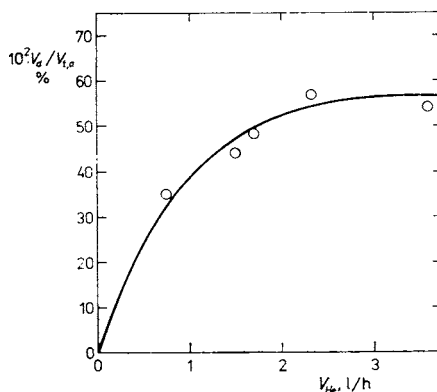
FIG. 4

Dependence of the fraction of restorated copper surface on the helium flow-rate. Catalyst R 3—11 (BASF), $S_{Cu} = 44\ m^2\ g^{-1}$, $t_{ads} = t_{des} = 100°C$, $\tau_{des} = 15$ min

desorbed oxygen depends on the experimental conditions during desorption but also on the temperature of decompositive N_2O adsorption (Fig. 5). b) The fraction of oxygen $(V_d/V_{t,a})$ which desorbs under the given conditions $(t_{des} = 100°C, \tau_{des} = 15 \text{ min})$ decreases with increasing temperature in the range of -20 to $+120°C$ (Fig. 6). c) The reversibly bonded fractions of O_{ads} are approximately constant and do not depend on the course of oxygen desorption (Fig. 7). Nevertheless, the rate of oxygen desorption depends on the temperature of the decompositive N_2O adsorption.

The finding c) is in good agreement with LEED results reported by Ertl[15,16] who have found that more stable species O_{ads} are formed on a copper surface at higher temperatures. The enhanced thermal stability of oxygen adsorbed after the decompositive N_2O adsorption at higher temperatures led us to an attempt to passivate or stabilize the copper surface with respect to atmospheric oxygen. The sample of copper powder with an adsorbed oxygen layer $(t_{ads} = 100°C)$ was heated up to approximately 150°C during 2 minutes. At this temperature, the surface was further saturated by N_2O introduced in several pulses. Under these conditions, a limited amount of N_2O was decomposed on copper (the rest-peak have not appeared) and the total amount of oxygen corresponded approximately to two atomic layers. The described treatment of the surface caused a stabilization of O_{ads}. When helium was passed
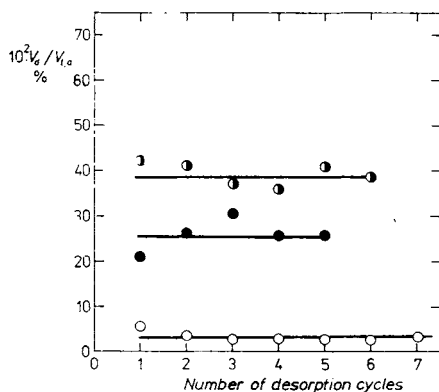

FIG. 5

Dependence of both fraction of restorated copper surface and the temperature of decompositive N_2O adsorption on the number of desorption cycles. $t_{des} = 100°C$, $\tau_{des} = 15 \text{ min}$, 1.67 l h^{-1} He, ○ sample I-3, $t_{ads} = 100°C$, ● sample I-3, $t_{ads} = 80°C$, ◑ sample II-3, $t_{ads} = 20°C$
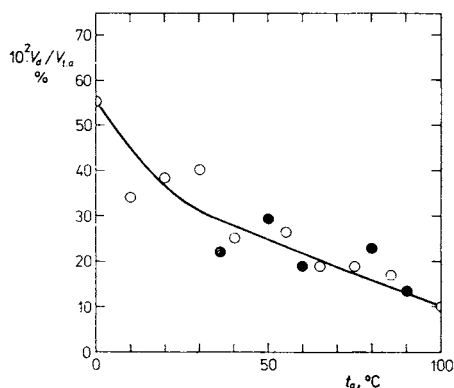
FIG. 6

Dependence of the fraction of restorated copper surface on the temperature of decompositive N_2O adsorption on the surface of copper powders. $t_{des} = 100°C$, $\tau_{des} = 15 \text{ min}$, 2.01 l h^{-1} He, ● sample I-2, ○ sample II-2

through the sample for one hour at 100°C, no desorption of O_{ads} was observed. The copper surface of this sample was fully inactive with respect to the decompositive N_2O adsorption, nevertheless it still strong reacted with atmospheric oxygen. The analysis of the above experiments shows that the weakly bonded species O_{ads} is responsible for the rest-peak occurence. This species desorbs under the conditions of decompositive N_2O adsorption from the surface permanently reactivating a part of the copper surface.

In order to support the idea of surface restoration by desorption, another indirect evidence was sought. The gases in helium stream desorbed from the oxygen covered sample had been led over pure copper sample. The fraction of the surface restored by desorption ($t_{des} = 100°C$) was practically equal to the blocked area of the second pure copper sample ($t_{ads} = 20°C$). However, this evidence is also not conclusive because of uncertainties regarding the quality of desorbing gases. The direct analysis of the desorbing gases released after concentration from getter, was oxygen evidence negative. To the same result arrived Evans and coworkers[10]. However, contrary to their experimental results we were observing the rest-peaks not only on the supported catalyst, but also on the pure copper powders and the size of peaks from both types of the copper samples were quite comparable. With respect to these results we cannot accept that a cause of the rest-peak is the bulk oxidation conditioned by presence of certain metal oxides as is suggested by Evans et al.[10]

Temperature Dependence of the Amount of Adsorbed Oxygen

The innovated procedure was used for determination of the temperature dependence of the amount of oxygen adsorbed. The conditions of the procedure recommended and used are listed in Table IV. The results are presented in Fig. 8. Each point
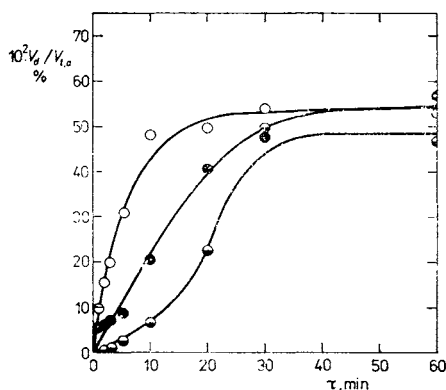
FIG. 7

Dependence of the fraction of restorated copper surface on both the time and the temperature of decompositive N_2O adsorption. $t_{des} = 100°C$, $2·4\,l\,h^{-1}$ He, ○ sample I-1, $t_{ads} = 20°C$, ● sample I-2, $t_{ads} = 20°C$, ◑ sample I-3, $t_{ads} = 100°C$

represents average value of three measurements. The dependence obtained is linear in the temperature range of −20 to +90°C. The results of all experiments in the range of −18 to +120°C were statistically treated by Eq. (1). The values of the amount of oxygen adsorbed in the range of 90 to 125°C were atributed to the temperature of 90°C. In this region the adsorbed amount is constant and is independent of the temperature because the monolayer is filled up.

$$K_T = \left(b T_{ads} + a\right) . 10^{19} . \tag{1}$$

For Eq. (1), the following parameters were calculated from 93 experiments: $b = (2{\cdot}467 . 10^{-3})\,m^{-2}\,K^{-1}$ and $a = -0{\cdot}199\,m^{-2}$. K_T corresponds to the number of oxygen atoms adsorbed per m^2 of the copper at the temperature T_{ads}. By means of calculated values of a and b, the lines in Fig. 8 were drawn. The reliability limits are given by dotted lines. The analysis of larger series of data has shown the relative error at 100°C is approximately half of that at 20°C. The higher error observed at 20°C may be caused by the temperature dependence of chemisorption while, in the region of 90 to 125°C, the adsorbed amount is independent of the temperature. Furthermore, the whole surface is covered by oxygen at 100°C and the adsorbed amount is therefore insensitive to the changes in the energy distribution of copper surface atoms. Obviously the reproducibility of this distribution is low in the preparation of dispersed copper phases. The value of K_T (363 K) calculated from Eq. (1)
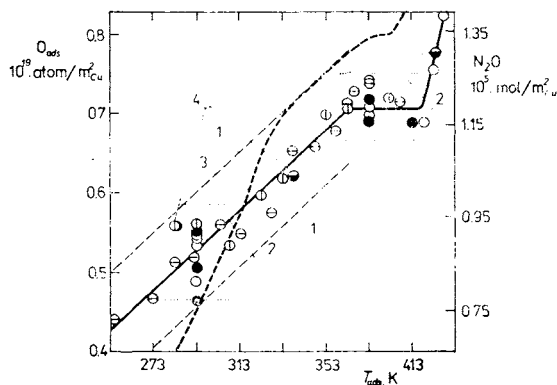

FIG. 8

Dependence of the amount of adsorbed oxygen on the temperature of decompositive N_2O adsorption, 1 limits of reliability, 2 maximum deviations (δ_i) of constants K_T (363 K) and K_T (293 K) from the average value $\delta_1 = \pm 5{\cdot}74$ and $\delta_2 = \pm 11{\cdot}24$, 3 dependence reported by Scholten and Konvalinka[1], 4 ◖ experimental points published by Evans et al.[10] ① average value of samples I-1 till I-3, ◒ average of samples II, ○ average of samples III, ● average of samples IV

TABLE V

A specific copper surface area and a mean size of copper particles in some industrial catalysts

Catalyst	Manufacturer	Specific copper surface area $m^2\ g_{Cu}^{-1}$	Mean size of copper particles, nm[a]		Relative error $10^2 . \Delta\langle d\rangle/\langle d_x\rangle^b$, %
			$\langle d_x\rangle$	$\langle d_y\rangle$	
K 3—10	BASF, F.R.G.	110·5	6·1	6·6	+8·2
R 3—11	BASF, F.R.G.	48·5	13·9	12·8	−7·9
NA	ZCH Oswięcim, Poland	29·8	22·6	18·0	−20·4
NA-2T	ZCH Oswięcim, Poland	33·3	20·2	18·9	−6·4
Cu 1107T	HARSHAW Chemical Co., U.S.A.	23·7	28·4	24·5	−13·7
Cu 1808T	HARSHAW Chemical Co., U.S.A.	31·2	21·6	—	—
Cu 122/2	HARSHAW Chemical Co., U.S.A.	69·6	9·6	11·2	+16·7
N 202D	NIKKY Chemical Co., Japan	43·5	15·5	14·2	−8·4

[a] $\langle d_x\rangle$ Value obtained from chemisorption measurements, $\langle d_y\rangle$ value calculated by means of X-ray line-broadening data; [b] $\Delta\langle d\rangle = \langle d_y\rangle - \langle d_x\rangle$.

to be $(0.697 \pm 0.040) \cdot 10^{19}$ and error in this value is equal to $\pm 5.74\%$. This represents the maximum error established in 29 experiments in the temperature range of 90 to 125°C. The constant $K_T(363 \text{ K})$ is in fair agreement with the value of $0.72 \cdot 10^{19}$ determined by Evans and coworkers[10]. The same constant published by Scholten and Konvalinka[1] is a little higher $(0.8 \cdot 10^{19})$.

There is a good quantitative agreement with papers[1,10] in which a temperature dependence was observed. These publications confirm that the amount of oxygen adsorbed depends linearly on the temperature range of 20 to 90°C. However, there is another group of investigators[5−7,11,12] who have found no substantial change in oxygen uptake by copper in the comparated temperature interval. In their opinion a sharp increase in N_2O decomposition exclusively indicates the onset of bulk oxidation in spite of very low temperature, 80°C (ref.[6]) or 70°C (ref.[7]). It is remarkable that the amount of oxygen adsorbed necessary to cover 1 m² of copper is in latter group of papers[5,6,11] almost of 30% smaller than in both present paper and papers[1,10] with observed temperature dependence.

Pulsed Experiments on Copper-Based Catalysts

The described procedure has been applied in the determination of specific area of a series commercial supported copper catalysts. The copper surface area S_{Cu} was calculated from Eq. (2)

$$S_{Cu} = A_N N_A / K_T(293) \, w \, . \tag{2}$$

The amount A_N was established from the sum of N_2 peak areas after the rest-peak has been substracted from all peaks except the first one. The used modification of both the procedure and calculation which takes into account the partial reactivation on surface during measurement served to increase the accuracy of the method.

The results obtained are shown in Table V. A good agreement in $\langle d \rangle$ values determined by two independent methods (chemisorption, X-ray line-broadening) supports the suitability and applicability of the proposed innovated procedure for determination of the specific copper surface area also in supported copper catalysts. However, when applying the decompositive N_2O adsorption to an unknown and still non tested catalyst, all principles ensuring the correctness of the chemisorption measurements on the metal surface of supported catalysts should be considered. This principles were clearly formulated by Scholten[2].

LIST OF SYMBOLS

a	constant in Eq. (1), m^{-2}
A	amount of oxygen adsorbed, mol
A_N	corrected amount of N_2 released by decompositive N_2O adsorption at temperature of 100°C, mol
$\langle A_{Cu} \rangle$	average area of copper site, nm²

b	constant in Eq. (I), $m^{-2} K^{-1}$
$\langle d \rangle$	mean size of copper particles, nm
$\langle D_{Cu} \rangle$	average copper surface atom density, atoms m^{-2}
$K_T(T)$	number of oxygen atoms adsorbed on 1 m^2 of copper surface area at the temperature T, K
N_A	Avogadro constant, $6 \cdot 023 . 10^{23}$ molecules per mol
S_{Cu}	copper surface area per gram copper, $m^2 g^{-1}$
$V_d / V_{t.a}$	volume of oxygen adsorbed after a restoration of copper surface related to that one adsorbed at temperature t, —
t_a, t_{ads}, T_{ads}	temperature of the decompositive N_2O adsorption, °C, K
t_{des}	temperature of desorption, °C
w	weight of copper, g
x, y	symbols related to chemisorption measurements and X-ray broadening data respectively
τ_{des}	time interval of a desorption or a restoration of copper surface area by helium stream, min
Θ_1	surface coverage, corresponding to a surface stoichiometry $Cu_{surf}/O_{ads} = 1$, for $\Theta_1 = 1$
Θ_2	saturated coverage to be 1 for surface stoichiometry $Cu_{surf}/O_{ads} = 2$
Θ_{ch}	number of oxygen atoms adsorbed per pair of copper atoms ($Cu \cdots Cu$) (surf)

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