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Determination of the Specific Copper Surface Area by Chromatographic Technique

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A method of determining the specific copper surface area by chromatographic technique has been suggested and experimentally checked. The value of surface coverage $\vartheta = 0.35$ agrees well with the experimental values determined by this method and proves that the decomposition of N_2O at room temperature is adequate for determining the specific copper surface area. A well defined value, however, was obtained only up to a temperature of 60°C, which is in contradiction to some previously reported results.

I. INTRODUCTION

For purposes of studying, forecasting, or elucidating the catalytic properties of mixed catalysts, in which the active component is a metal, the specific surface area of this active component is a very useful physical characteristic. As copper catalysts usually contain more than 20% of the active component, chemisorption is practically the only suitable method for determining the specific copper surface area as a result of their lower activity.

Only recently (*1*) has a suitable method been recommended, exploiting selective chemisorption, for measuring the copper surface area. The authors of this method have shown that the decomposition of N_2O on a copper surface area according to the equation

$$N_2O \rightleftarrows N_2 + O_{ads} \text{ at } 20°C \qquad (1)$$

is an adequate method for measuring the specific copper surface area. The experiment itself was carried out in a classical volume adsorption apparatus and the amount of nitrogen released in the course of reaction (1), which is the measure of the adsorbed amount, was determined by measuring the residual pressure of N_2 after freezing out the excessive N_2O at 78°K.

In this study an attempt has been made to apply the measurement of copper surface areas by the method of Osingna *et al.* (*1*) to the chromatographic technique for measuring of the specific surface area, currently used today.

The nitrous oxide was fed into the carrier-gas–catalyst system in pulse by means of a six-way feeding cock, and its excess was removed from the He–N_2 gas mixture by cooling to 78°K, or at 20°C by irreversible sorption on an activated molecular type 5 A sieve. The N_2, released by the reaction, was determined from the change of the thermal conductivity of the He–N_2 gas mixture.

II. EXPERIMENTAL METHODS

The apparatus used for determining the specific copper surface area (Fig. 1) is similar to the conventional apparatus used for gas chromatography. The apparatus as a whole is practically made of glass (there are no rubber joints), and the glass–metal joints have been executed in a manner indicated by Fig. 2. The purity of the gases, as well as the tightness of the joints with regard to the diffusion of air oxygen, were investigated by modified analyzer (*2*), which determined the O_2-content continu-

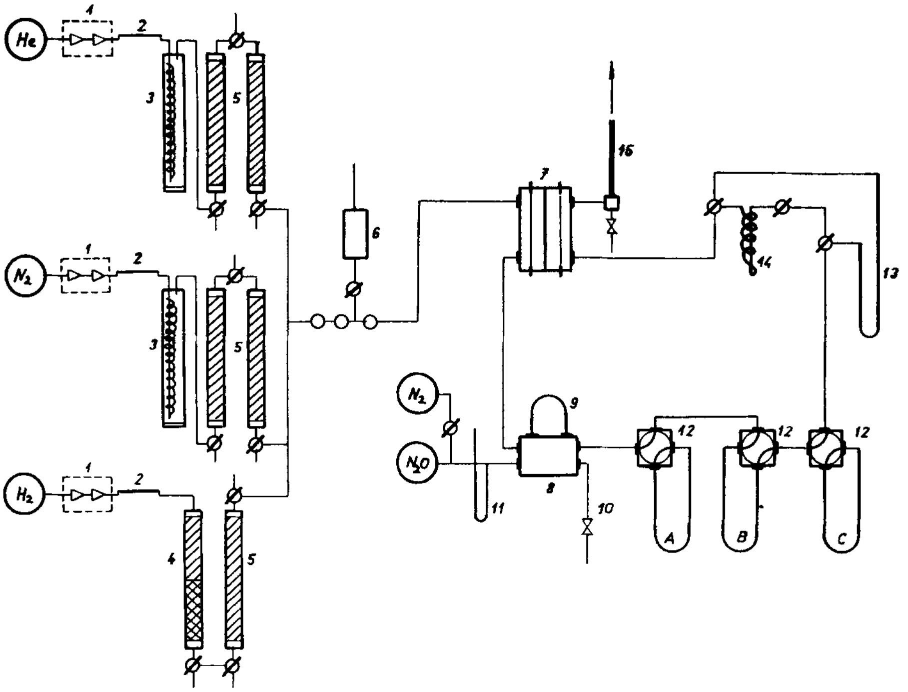

FIG. 1. Apparatus for measuring the specific copper surface area by chromatographic technique: 1, accurate manostat; 2, capillary; 3, liquid purifier; 4, catalytic purifier; 5, tower with molecular sieve; 6, oxygen analyzer; 7, conductivity detector; 8, six-way feeder cock; 9, feeder capillary; 10, throttling valve; 11, manometer; 12, four-way cock; 13, analytic column; 14, mixing chamber; 15, film flow-meter; A, B, C adsorption vessels.

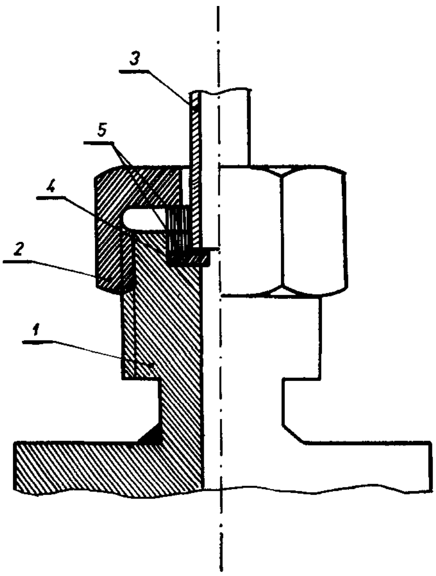

FIG. 2. The way of joining metal and glass: 1, body of cock; 2, flange nut; 3, glass pipe; 4, Teflon sealing; 5, O-rings of silicon rubber.

ously. The carrier gas was deprived of oxygen by being passed over a wet liquid purifier and dried in two towers with molecular sieves. The N_2O was purified of N_2 and O_2 by rapidly evaporating a certain amount of liquid N_2O by expansion from a bomb. The purity of N_2O was checked chromatographically (using the same apparatus); if about 5 ml of N_2O were fed into the carried gas (He) the thermal-conductivity detector showed no response after the separation of the N_2O in the analytical column even at the highest sensitivity. The samples investigated were placed in glass U-type columns with an internal diameter of 4–9 mm, which were connected to four-way metal cocks. The nitrous oxide, like the nitrogen, were fed into the apparatus by means of a six-way metal feeding cock.

The measurement. Description of a model experiment and the specification of the part of the apparatus which had the decisive significance for measuring the specific surface area. The copper powders were prepared by careful reduction of CuO directly in the measuring columns. The reduction was carried out at temperatures of 160–180°C (supported catalysts 180–210°C) by an H_2–N_2 mixture, the partial hydrogen pressure at the beginning of the reduction was 0.1 atm and at the end, 1 atm; and the total flow was 20 liters/hr. The samples A, B, and C (Fig. 1) were connected in series. The weights of the individual samples were between 0.2 and 0.8 g, and the reduction period in all cases was 2.5 hr. After reduction, all three samples (A,B,C) were rinsed by a flow of He (2.0–2.5 liters/hr) for a period of 15–20 min at 180°C, and then for 10–15 min at room temperature. The He-flow was then aimed so that it only passed over one of the samples, through the analytical column, and the measuring cell of the conductivity detector. The analytical column was of the U-type, it had a total length of 700 mm and an internal diameter of 12–14 mm. In the right-hand branch, about 100 mm from the bottom of the column the injections were made. In the course of freezing out the gas mixture (He, N_2O, N_2) by liquid nitrogen, part of the column was empty, and above the level of the liquid nitrogen a layer of glass spheres, 2 mm in diameter, was introduced. In working with the molecular sieve the analytical column was filled with the activated molecular type 5 A sieve, grain diameter 0.2–0.5 mm, with a layer length of 150 mm.

During the measurement itself the flow of the carrier gas was between 30 and 37 ml/min. The nitrous oxide was fed by rinsing the feeder capillary by a stream of the carrier gas; the magnitude of one of pulses was between 1.5 and 4.5 ml, according to the specific copper surface area. In working with the molecular sieve the N_2O pulse was introduced into the system at a pressure of 50–150 mm H_2O. The diameter of the feeder capillaries was 2–3 mm, and all were of a simple U-shape. The joints between the feeder and four-way cocks were of the same diameter (2–3 mm). The lengths of these joints were minimal as allowed for by the assembly and the arrangement of the apparatus.

The relation between the detector response and the amount of N_2, released during reaction (1), was determined by nitrogen calibration using the pulse technique, with the help of a six-way feeder cock.

The specific copper surface area was calculated using the values given previously (*1*), which define the amount of N_2O required to cover 1 m^2 of copper surface area:

$$0.176 \pm 0.010 \text{ ml (NTP) of } N_2O/m^2 \text{ of Cu.}$$

The surface coverage ϑ is defined by Osinga *et al.* (*1*) as the number of oxygen atoms adsorbed per surface atom of copper, and under the assumption that planes (100), (110), and (111) are represented equally in the copper surface area, they found that $\vartheta = 0.35 \pm 0.02$.

The measurement of the specific copper surface areas (only with pure copper powders), for the purpose of checking the method studied, was carried out with the same apparatus by means of physical N_2-sorption at 78°K. Instead of the analytical column, a three-way cock was used to connect a mixer for adjusting the total flow of the gas, which is prone to change as a result of the desorbing gas, and to obtain a symmetric and less sharp peak. For computing the specific copper surface area by physical N_2-sorption the value $\sigma_{N_2} = 16.2$ Å^2 was used.

III. Results and Discussion

The successful application of the method, described by Osinga *et al.* (*1*), by means of chromatographic technique, is conditioned by:

the high purity of the gases used,

the perfect separation of N_2O from the flow of the He–N_2 gas mixture

the sufficiently high rate of the $N_2O \rightleftharpoons N_2 + O_{ads}$ reaction (1).

For the error in determining the copper surface area, due to the oxygen in the carrier gas, when the total copper surface area is equal to or over 1 m^2, to be less than 5%, the oxygen content of the carrier gas, under experimental conditions (Sect. II), must be less than $3 \times 10^{-3}\%$ in volume. The oxygen content in the carrier gas can be decreased from the initial 0.05–0.15% in volume to 2–5 × 10^{-5}% in volume by passing the gas through the liquid purifier, described previously (*3*). However, the required purity was only achieved after the apparatus was modified (Sect. II) to exclude practically the possibility of diffusion of air oxygen into the carrier gas. In this connection it was found that the method of feeding in gases by means of an injection syringe for purposes of measuring metal surfaces, could not be used. Apart from the diffusion of air through the rubber stopper, already mentioned, difficulties are also caused by the fact that the residues of air in the injection syringe (especially of larger volumes) cannot be removed.

Two methods of removing nitrous oxide from the carrier gas flow were tested: freezing out and irreversible sorption on a molecular sieve. The separation by both methods was complete even at comparatively high linear flow rates (5.0 m/min). However, in measuring the actual specific surface area, it is necessary, besides removing the excessive N_2O, also to measure simultaneously the amount of N_2, which is released during the reaction with the copper surface area. To prove that during the separation of N_2O the N_2-response is not affected and that the amount of N_2 released has not been distorted, the conditions of the measurement itself were simulated by investigating and removing the N_2O from an He–N_2 gas mixture (partial pressure of N_2 about 150 mm Hg). In removing about 4–5 cm^3 of N_2O from the gas mixture the zero base line of the recorder began to oscillate, the deviations being positive as well as negative. The analysis of the said deviations (of the individual peaks) indicated that they were due to pressure and concentration changes caused by the rapid, but especially by the considerable change of the instaneous flow rate, which occurred in the course of removing the N_2O. Part of the N_2 concentration changes was due to occlusion or to the absorption of nitrogen; however as the latter is perfectly reversible it cannot affect the measurement itself but only affects the shape of the individual peaks. These undesirable deviations were practically removed after the total amount of N_2O fed in at a time was decreased and after the free volume between the freezer and the detector had been increased. The determination of the optimum amount of N_2O will be discussed elsewhere.

In the series of orientational experiments it was found that to cover a $\vartheta = 0.35$ copper surface area, seven or more N_2O pulses were required, although operations were carried out with a 100% excess of N_2O in each pulse (relative to the total copper surface area). The change in the reaction temperature in reaction (1) in the range from 20 to 60°C had practically no effect on decreasing the total number of pulses and on the change of the mutual ratio of areas of the individual peaks. At a temperature of 80°C the areas of the individual peaks increased considerably, and the total volume of the decomposed N_2O was approximately 100% higher than the volume required for covering $\vartheta = 0.35$. At this temperature, apparently, migration of oxygen atoms into the bulk phase of the copper powders occurs to a large extent.

This finding is in contradiction to the experimental values given by Osinga *et al.* (*1*). These authors have stated that the defined coverage ($\vartheta = 0.35$) can be executed with pure copper powders up to the temperature of 120°C, and with supported catalysts up to 100°C.

Not even the varying of the desorption time led to the decrease in the number of N_2O pulses; the desorption procedure, described in Sect. II guarantees a perfect removal of the H_2 from the copper surface area. The same magnitude of the third and seventh peaks excluded the possibility of applying the decelerating effect of the external and internal diffusion. This fact was also proved in another way. The change in the grain size in the range 1.0–0.25 mm had no effect on decreasing the number of pulses. A substantial reduction in the number of pulses (3–4) occurred after the samples had been carefully arranged in a vertical layer and after they had been shaken down well after the reduction. The sample investigated must not be freely placed at the bottom of the adsorption vessel, but it must be in a well-arranged layer, otherwise the bypassing has considerable effect.

The purpose of further experiments was to check the reproducibility of the method suggested. The results obtained are summarized in Table 1, and they indicate that the reproducibility is very good. The maximum deviation from the average value of the peak areas (this value is proportional to the amount of adsorbed oxygen) amounted to ±3.5 and ±6.5% with samples 1 and 2, respectively. Table 1 also shows that two pulses are required to cover the chemisorbed monolayer when the sample is in adsorption vessel A (Fig. 1); if the sample is in adsorption vessel B, 3–4 pulses are required. The change in order $(A \rightleftharpoons B)$ of the adsorption vessels together with the samples in respect of the direction of the gas flow, indicates that the number of pulses required to cover the monolayer depends on the position, or on the distance of the sample from the point where the N_2O enters the carrier gas. It was assumed that the cause of this behavior was the low partial nitrous oxide pressure in the location of the sample, which decreases after the feeding-in as a result of axial diffusion and of mixing. This hypothesis was proved experimentally. After the total free volume between the feeder cock and the sample bed had been decreased (Sect. II) and especially after the amount of N_2O fed in had been increased at a time (by about 50%), the monolayer was covered practically by a single pulse. This modification, however, had no effect on decreasing the amount of pulses when the separation of N_2O was carried out by irreversible sorption on a molecular sieve; three or more N_2O pulses were again required to cover $\vartheta = 0.35$. Only after the N_2O was being fed in under a pressure of 100–150 mm H_2O, which corresponds to the pressure gradient on the molecular sieve, the monolayer was covered after a single pulse.

The necessity of feeding in N_2O under increased pressure has its cause, like in the previous case, in the low partial pressure of the N_2O in the location of the sample

TABLE 1

Reproducibility of the Studied Method for Measuring the Specific Copper Surface Area[a]

Adsorption vessel A					Adsorption vessel B				
Sample no.	No. of pulses	Areas of individual peaks S	Total area S	Sorption temp (°C)	Sample no.	No. of pulses	Areas of individual peaks S	Total area S	Sorption temp (°C)
1	2	15.3 0.3	15.6	25	2	3	16.85 0.85 0.15	17.85	25
1^b	2	15.5 0.7	16.2	30	2^b	3	16.55 2.07 0.4	19.02	20
1^b	2	15.4 0.35	15.75	50	2^b	4	16.75 1.58 0.55 0.2	19.08	40
1^b	2	14.95 0.45	15.4	50	2^b	4	17.9 1.5 0.6 0.2	20.2	50
1^b	2	16.0 0.2	16.2	60	2^b	3	17.2 0.4 0.2	17.8	60
2^b	2	18.9 0.3	19.2	60	1^b	4	15.3 0.7 0.4 0.15	16.55	60

[a] Samples 1 and 2 were prepared by reducing the CuO powder in the way described in Sect. II.

[b] Samples 1^b and 2^b were obtained by regeneration using hydrogen at a temperature of 180°C for a period of 0.5–0.75 hr, of samples 1 and 2 after the reaction with N_2O had taken place.

bed. It also decreases as a result of axial diffusion, but its propelling force in this case is the difference in total pressures, the pressure of the carrier gas and the pressure of the N_2O enclosed in the feeder capillary.

It follows from the experimental findings that the optimization of the amount of N_2O depends on the hydrodynamic conditions of feeding in. The lower limit, i.e., the amount of N_2O which is at least required to cover $\vartheta = 0.35$ at a one-shot feed-in, depends on the size of the free volume between the feeder cock and the sample, on the manner of situation of the sample, on the gas flow rate, but also on the shape and especially the cross-section of the feeder capillary. Under the experimental arrangement and operational conditions, described in Sect. II, the minimum amount fed in at a time was approximately twice the theoretical amount. The upper limit of the amount of N_2O is limited by the size of the free volume between the sample and the freezer, but especially between the freezer and the detector. The free volume and the filled part of the analytical column guarantees the mixing of the gas mixture and equalizes the undesirable pressure and concentration gradients, which are due to N_2O separation. On the other hand, the size and shape of these parts is limited by the sensitivity of the detector. Under the present experimental conditions the free volume between the freezer and the detector was approximately 80 cm^3 and the upper limit of the fed in amount of N_2O was 5 ml.

The suitability and the applicability of the method studied for measuring the specific copper surface area was in the end assessed by comparison of specific surface areas, determined by the suggested and standard methods. As the standard, the method of thermal N_2-desorption was applied, which is being currently used. The results observed have been summarized in Table 2. In order to exclude any random effect from these measurements, 2–3 samples were investigated under the same conditions simultaneously (preparation of the samples, as well as the measurement of the specific surface area itself). The maximum deviation of the specific surface areas observed from their average value was lower than 4% with all sample series. This accuracy was achieved by both methods, which indicates not only a good reproducibility of the measurements, but also an excellent reproducibility of preparation of the samples. Even better agreement was achieved with samples which were prepared by mere regeneration of the samples measured (II–IIa, Table 2), which proves the conclusions of the orientational experiments.

The values of the specific copper surface areas, measured by two different methods, by the method of selective chemisorption and by the method of thermal N_2-desorption, however, differed considerably. The differences in the values of specific surface areas, however, do not display a constant error, but they cover a considerable range. This large range, however, does not display a random scatter over the whole interval, but two categories of deviations, coinciding with the groups denoting the order of application of the methods used in measuring the specific surface area (Table 2, column 12). The difference in the specific surface areas is expressed in Table 2 as a relative deviation of the value of the specific surface area, measured by selective chemisorption, relative to the value obtained by the standard method.

The samples which were first investigated by physical N_2-sorption (samples 1–3, 9–11) display a comparatively high relative deviation. The values of the specific surface areas of the samples, which were first subject to selective chemisorption (samples 7–8, 12–14) agree well with the values obtained by the other method. The real reason for the differing results, considering the different order of application of the methods used for measuring the surface areas, is, according to the authors' opinion the different times of exposure of the pure copper surface area in a medium containing molecular oxygen. The samples first subject to physical sorption were acted upon by oxygen for a period of 5–6 hr; whereas, when the order was reversed, the samples were only subject to the action of molecular oxygen for a maximum of 1 hr.

TABLE 2

SPECIFIC SURFACE AREA OF COPPER POWDERS DETERMINED BY METHODS OF CHEMISORPTION AND PHYSICAL SORPTION

Sample no.	Adsorption vessel	Method of preparing samples[a]	Chemisorption S (m^2/g)	$\bar{S}$	$\bar{S}_I$ $\bar{S}_I = \Sigma\bar{S}/n$	Max error (%)	Physical sorption S (m^2/g)	$\bar{S}$	Max error (%)	Relative deviation (%)	Order in applying the methods	
											I	II
1	A	I	3.60				4.84					
2	B		3.67	3.7	3.7	3.5	4.62	4.67	3.5	−20.8	FS	CHS
3	C		3.83				4.54					
4	A	II	5.71									
5	B		5.99	5.93							CHS	—
6	C		6.10		5.98	2.5						
7	B	IIa	6.04				5.67					
8	C		6.09	6.07			5.74	5.70	0.7	+6.0	CHS	FS
9	A	III	6.91				8.22					
10	B		7.25	7.14			8.58	8.50	3.5	−16.0	FS	CHS
11	C		7.27		7.21	2.0	8.71					
12	B	IIIa	7.28				7.57					
13	C		7.36	7.32			7.62	7.59	0.4	−3.5	CHS	FS
14	A	IV	4.12				4.28			−3.7	CHS	FS

[a] I, reduction carried out by a mixture of $H_2:N_2 = 1$; temp, 180°C; II, reduction carried out by method described in Sect. II; IIa, samples from II regenerated after measurement (Table 1); III, reduction carried out by method described in Sect. II, different CuO charge; IIIa, reduction carried out in the same way at in III; after the reduction the samples were kept under a cold flow of H_2 for 12 hr, prior to measuremens they were re-reduced under heat; IV, sample after reduction thermally treated in a flow of H_2 at 400°C.

The fact that always the first (A) sample of the series of parallelly measured samples displayed specific surface areas about 5% smaller than both the other samples (B, C), agrees with this opinion. During desorption samples A, B, C are interconnected in series, so that the first sample apparently captures all the oxygen contained in the carried gas; the 5% deviation also agrees with the computed size of the measurement error, due to the oxygen content in the carrier gas Sect. II.

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