NOTES

The Determination of the Specific Copper Surface Area in Catalysts*

It has been shown (1) that copper catalysts are highly selective in the hydrogenation of edible oils and fats. To study the behavior of the catalysts in this process, it is necessary to know the specific metal surface area. In practice chemisorption forms an ideal basis for surface determinations, especially for metals. A prerequisite of this method is that the adsorbate forms a monolayer on the surface and that there is a relationship between the number of molecules adsorbed and the number of surface atoms.

As far as is known no good method is given in the literature for the determination of copper surface areas. Some investigators used hydrogen (2), although this method is very doubtful (3, 4). Dell et al. (5) studied the adsorption of CO, O_2 and the decomposition of N_2O on copper powders. They reported that after decomposition of N_2O the oxygen coverage was 20–25% of a monolayer, the same value was found for the adsorption of CO.

We have found that the decomposition of N_2O at room temperature is an adequate method for measuring specific copper surface areas.

The adsorption measurements were carried out using a conventional volumetric adsorption apparatus. During the adsorption measurements there is no change in

pressure, as N_2O decomposes on the copper surface according to the reaction

$$N_2O \rightleftarrows N_2 + O_{adsorbed}$$
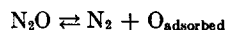
The amount of nitrogen formed was determined according to Dell et al. (5) by freezing out at 78°K the excess of N_2O in a "cold-finger" for 2 hr and measuring the residual nitrogen pressure. It was ascertained that this procedure did not give rise to a systematic error. The copper powders were prepared by careful reduction of copper oxide at 180–200°C. In the adsorption behavior and in the degree of reduction (>99.5%) no changes could be observed after one day of reduction. After reduction the hydrogen was pumped off at 180°C for 2 hr. The surface areas of the copper powders were determined by adsorption measurements with nitrogen at liquid nitrogen temperature using a σ value of 16.27 Å² for the nitrogen molecule. The copper surface areas varied between 10.5 m²/g Cu and 14.8 m²/g Cu.

The decomposition reaction of N_2O was not only studied on pure copper but also on a copper-on-carrier catalyst.

Table 1,A shows the results of the adsorption measurements of N_2O on copper powders at various temperatures and at an initial N_2O pressure of about 600 mm Hg. No influence of the initial N_2O pressure on the adsorption could be observed, provided that enough N_2O is present to cover the copper surface with a monolayer of oxygen.

The surface coverage θ is defined as the number of oxygen atoms adsorbed per surface copper atom. For the calculation of

TABLE 1

RELATIONSHIP BETWEEN TEMPERATURE AND DECOMPOSITION OF N_2O ADSORBED ON COPPER (A)
AND SUPPORTED COPPER (B AND C)

A		B		C	
Temperature of adsorption (°C)	θ	Temperature of adsorption (°C)	Cu surface area (m²/g Cu)	Temperature of adsorption (°C)	Cu surface area (m²/g Cu)
20	0.35 ± 0.02[a]	20	100 ± 10	$20 \rightarrow 150$	100 ± 10
80	0.35 ± 0.02[a]	100	106 ± 10	$20 \rightarrow 180$	100 ± 10
120	0.35 ± 0.02[a]	120	$270 \rightarrow 1152$	$20 \rightarrow 250$	786
150	1.9 ± 0.8	150	$191 \rightarrow 1155$		
180	> 4.0				
220	± 10				

[a] 0.176 ml (NTP) N_2O/m^2 Cu.

the number of surface atoms per m² of copper surface area, it was assumed that the 100, 110, and 111 planes are equally present in the surface. This assumption leads to a mean surface area for a copper site of 7.41 Å², corresponding with 1.35×10^{19} copper sites/m². From Table 1,A it appears, that up to an adsorption temperature of 120°C, θ is 0.35 ± 0.02, corresponding to a consumption of 0.176 ± 0.010 ml (NTP) N_2O/m^2. This value is in rather good agreement with the picture of the adsorption on different crystal faces of copper proposed by Pritchard (6). Dell et al. (5) found a value for θ of 0.20–0.25. We believe that there are two reasons for this discrepancy, namely, (1) they use 6.8 Å² for the mean surface area of a copper site instead of 7.41 Å²; (2) we use for the determination of the surface area of our copper powders nitrogen adsorption, whereas Dell et al. used krypton adsorption. They assume a σ value of 21 Å² while many authors (7, 8, 9) propose a value of ± 15.4 Å². We have this matter under investigation.

Correction of the θ found by Dell et al. for both factors, gives a value of 0.30–0.37, which corresponds with our value. Furthermore Dell et al. report that after heating a copper powder at 320°C the surface coverage (θ) dropped to 0.07–0.10. This finding could not be confirmed by us; our θ remains constant.

At adsorption temperatures above 120°C (Table 1,A) we could not establish well-defined values for θ, due to the fact that the reaction is not restricted to the surface any longer. At these adsorption temperatures a heat explosion occurred and a great influence of the amount of copper weighed-in could be observed.

The results of the adsorption measurements with N_2O on a copper-on-carrier catalyst are given in Table 1,B. For the calculation of the specific copper surface area we used the previously mentioned value of 0.176 ml (NTP) N_2O/m^2 Cu. It appears that up to temperatures of 100°C a reproducible value for the specific copper surface area was found. Above this temperature we could not establish well-defined values again due to further reaction. In some cases complete oxidation of the metallic copper was already attained at 120°C. It was established that no measurable adsorption took place on the carrier or on copper oxide.

The temperature at which further reaction sets in is about 20°C lower than for the pure copper powders (Table 1,A). This can be easily understood when it is realized that the copper surface area per gram copper is about 10 times higher for the copper-on-carrier catalyst, so the total heat of adsorption, instantly generated, is relatively higher, resulting in a higher, but unknown temperature of the copper surface. This phenomenon can be proved with the results mentioned in Table 1,C, in which cases the adsorptions were carried out initially at 20°C after which the temperature

was increased. In these cases further reaction could not be observed at temperatures up to 180°C.

From our results we may conclude that the decomposition of N_2O at room temperature is an adequate method for the determination of specific copper surface areas.

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The Influence of Oxygen on the Catalytic Reduction of Nitric Oxide by Ammonia

Investigations on the heterogeneous catalytic reduction of nitric oxide, especially by means of hydrogen and carbon monoxide, have already been treated in a series of papers. Only a few authors (1–4), however, have studied the catalytic reaction of nitric oxide with ammonia, and their papers, moreover, present only qualitative conclusions.

Only Mikhailova (5) has investigated in some detail the course of the reaction of nitric oxide with ammonia on a platinum filament as a catalyst. The experiments were performed in a static apparatus with a circulating gas mixture at a total pressure of 10–20 torr and at temperatures of 500–530°K. Evaluating the results of her measurements, the author formulated the hypothesis that the reaction proceeds, in the absence of oxygen, between molecules of ammonia and nitric oxide adsorbed on adjacent active centers of the catalyst. From the fact that the original activity of the Pt filament is reduced by heating in an oxygen atmosphere or in air the author concluded—not quite exactly—that the reaction is inhibited by oxygen.

The influence of the presence of oxygen on the catalytic reaction of nitric oxide with ammonia has not been studied yet, though the reaction also has some practical importance. It is, however, commonly known that from a mixture of nitrogen oxides ($NO + NO_2$) with oxygen the nitrogen oxides are reduced by ammonia preferentially, i.e., that ammonia reacts selectively.

To be able to explain this phenomenon and the influence of oxygen in the reaction mentioned the authors of the present note investigated the course of the reaction of ammonia with nitric oxide alone, as well as that of the reaction in the presence of oxygen.

EXPERIMENTAL

The investigations on the reaction $NH_3 + NO \rightarrow N_2 + H_2O$ were performed on Pt-