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The Adsorption of Nitric Oxide on Copper Oxides*

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Adsorption isotherms and rates were measured for NO chemisorption on supported and unsupported samples of copper oxide in the 26–140°C temperature range. The adsorption behavior on cupric oxide is well described by Freundlich isotherms. The adsorption rates on the cupric oxide are represented by two intersecting segments in the coordinates of the Elovich equation.

On cuprous oxide at room temperature the oxidation of the surface is superimposed onto the adsorption phenomenon. Nevertheless, it could be deduced that the surface cuprous ions chemisorb nitric oxide molecules very slowly, if at all. This experimental fact is explained by the absence in $Cu^+(d^{10})$ of an unpaired *d*-orbital required for the accomodation, upon chemisorption, of the antibonding electron of the NO molecule.

INTRODUCTION

This communication is one of a series dealing with NO chemisorption on supported and nonsupported transition metal oxides. Similar studies on chromium oxides (*1*), iron oxides (*2*), and nickel oxide (*3*) have been published previously.

EXPERIMENTAL METHODS

Two supported samples and one unsupported sample of copper oxide were employed as the adsorbents. The supported samples were made by impregnating Kaiser KA-201 alumina ⅛ in. diameter spheres in a solution of copper nitrate, drying overnight at 120°C, and calcining at 650° for 6 hr. One catalyst contained 8.89 and the other 0.816 wt % of Cu; they were designated SC1 and SC2, respectively. Unsupported CuO (designated SC3) was prepared by the decomposition of pure grade $Cu(NO_3)_2 \cdot 3H_2O$ at 400°C overnight. The chemisorption of NO on the diluted sample (SC2) and the pure CuO (SC3) served to establish the ratio of adsorbate to the surface copper atoms in these two limiting cases. The total BET areas of SC1, SC2, and SC3 were 168, 171, and 0.97 m^2/g.

The catalysts were prepared in the oxidized state by heating to a constant weight in 10 Torr of oxygen at 450°C; in the reduced state by heating at the same temperature, in 30 Torr of a gaseous mixture of 10% CO and 90% CO_2 which is, under these conditions, in equilibrium with solid Cu_2O (*4*). Weight changes measured for the SC1 sample between the oxidized and reduced states correspond to an almost complete reduction of CuO to Cu_2O: the expected weight change for 1 g of SC1 is 11.18 mg and the measured one was 10.2 mg. Oxidation of SC1 takes ~1 hr while the complete reduction requires in excess of 8 hr. Nitric oxide adsorption after repeated oxidation–reduction cycles was reproducible.

Matheson Research Grade gases were used with the exception of NO, which was purified according to the previously published procedure (*2*). The apparatus was built around a Cahn Electro-balance. The measurement procedure was the same as that described in detail earlier and corrections were also applied for the adsorption

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on the support and for the shrinkage of the absorbent during the course of the study (2, 3).

RESULTS AND DISCUSSION

A. Adsorption Isotherms

The Freundlich isotherms for sample SC1

$$q = cp^{1/n} \tag{1}$$

are plotted in Fig. 1. Here q is the amount adsorbed at pressure p; c and n are temperature dependent constants, whose values are given in Table 1.

The logarithmic, refined form of the isotherm (3, 5), is given by the equation:

$$\log q = \log q_m + \frac{RT}{H_m(1 - rT)} \log a_0 + \frac{RT}{H_m(1 - rT)} \log p, \tag{2}$$

where

$$H_m = \frac{nRT}{(1 - rT)} = \text{constant}. \tag{3}$$

The terms in the equation are: q = the amount adsorbed at pressure p, q_m = amount adsorbed at monolayer coverage, T = temperature of the isotherm, R = gas constant, H_m = heat of adsorption at $\theta = 0.37$, a_0 = a constant which defines the pressure at monolayer coverage ($1/a_0$); r is defined by Eq. (3), being an adjustable parameter, due to Halsey (6), introduced to assure the constancy of H_m with temperature. As shown in Table 1, without the introduction of parameter r, there is a gradual decrease of H_m with T as was the case in the NO chemisorption on supported nickel oxide (3).

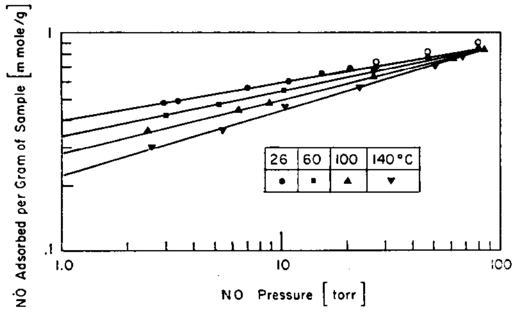

FIG. 1. Adsorption isotherm for NO on supported copper oxide (SC1). (○) Before correction for adsorption on the support.

TABLE 1
PARAMETERS OF FREUNDLICH ISOTHERMS FOR NO ADSORPTION ON SUPPORTED COPPER OXIDE (SC1)

T(°K)	n	nT	$H_m = \frac{nRT}{(1 - rT)^a}$ cal/g mole	c (mmole/g)
299	5.72	1705	5082	0.398
333	4.82	1610	5087	0.338
373	4.09	1525	5187	0.280
413	3.33	1380	5080	0.223
	Av H_m		5109	

[a] $r = 1.12 \times 10^{-3} [°K]^{-1}$.

Figure 2 shows the logarithmic decline with coverage of the isosteric chemisorption heat. The circular points give the values derived from the relationship $H_\theta =$

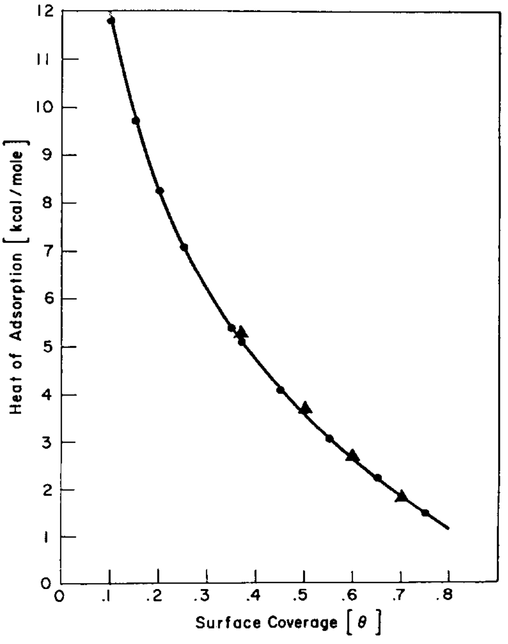

FIG. 2. Heat of adsorption vs surface coverage for NO adsorption on supported copper oxide (SC1). (○) Calculated from $H_\theta = -H_m \ln \theta$; (△) From Clausius-Clapeyron equation.

$-H_m \ln \theta$, using the H_m value from Table 1. The triangular points were obtained by applying directly the Clausius-Clapeyron equation to the isotherms of Fig. 1. One has to remember that, strictly speaking, the logarithmic decline of H_θ holds only in the limit of middle coverages $0.1 < \theta < 0.8$. The agreement is indicative of the internal consistency of the data. At the oxidized surface, the amount adsorbed at monolayer coverage is $q_m - 0.84$ mmole NO/g, as given by the intersection point of the isotherms in Fig. 1. The monolayer coverage is attained at $p = 1/a_0 = 85$ Torr.

For the reduced surface of the SC1 catalyst (Cu_2O), it was not possible to obtain equilibrium adsorption data because of the slow oxidation of Cu^+ to Cu^{2+}. For instance, at room temperature and $p_{NO} = 12$ Torr, the sample continues to gain weight even after 98 hr at a rate of 0.05 mg NO/hr. At higher temperatures and pressures, the steady rate of weight gain was even higher, as one would expect, owing to the accelerated oxidation.

In an experiment performed to establish the extent of oxidation of cuprous oxide to cupric oxide, NO was brought into contact with the reduced sample SC1 at room temperature at $p_{NO} = 85$ Torr. After 9 days, the steady rate of weight increase was 0.06 mg/hr. The total weight gain, at that juncture, was 29 mg/g (0.974 mmole/g) which exceeds the monolayer coverage by 4 mg/g. Upon desorption, the sample retained 92% of the weight gain after 5 hr pumping at room temperature, 45% after 3 hr at 150°C, and 21% corresponding to 6.13 mg/g, after pumping overnight at 450°C. The oxidation at 450° in 10 Torr of O_2 resulted in an additional weight gain of 4.02 mg/g for a total of 10.15 mg. This is almost exactly the weight gain observed in the oxidation–reduction cycle between the Cu_2O and CuO states.

Hence, out of the 10.15 mg, the 4.0 mg excess weight originally taken up represents the minimum level of room temperature oxidation. The upper limit is given by the 6.13 mg retained after the long time desorption. This corresponds to between 40 and 60% of total oxidation from Cu^+ to Cu^{2+}. As shown below, close to 60% of the Cu atoms in SC1 are exposed on the surface.

B. Adsorption Rates

The adsorption rate of NO on oxidized copper oxide is well represented by the Elovich equation. The experimental data at 26, 60, 100, and 140°, taken at $p_{NO} \sim 3$ Torr, are plotted in Fig. 3 in the coordinates of the integrated Elovich equation,

$$q = (2.3/\alpha) \log(t + t_0) - (2.3/\alpha) \log t_0, \quad (4)$$

where t_0 is an integration constant, and α is a temperature dependent constant, characterizing the chemisorption rate. The plots were linearized by assigning t_0 values of 15, 15, 20, and 35 sec at 26, 60, 100, and 140°C, respectively. The Elovich plots consist of two intersecting straight-line segments at each of the four temperatures. Table 2 gives the θ values at the point of intersection and the α values for each segment. The θ at intersection decreases with temperature, as was also the case with the supported nickel oxide (*3*). While α_1 increases with T, α_2 decreases and the ratio of α_2 to α_1 goes from values higher than unity to fractional values. For the first segment of the Elovich plots, the temperature coefficient of the adsorption rate of NO is negative. This was observed previously in all cases of NO adsorption on supported metal oxide catalysts. The temperature coefficient of the NO adsorption rate in the second segment is positive.

TABLE 2

Coverage Values at the Intersection of Two Segments of Elovich Plots and α Values for the Two Segments of NO Chemisorption Kinetics on Oxidized Copper Oxide (SC1)

		$\left(\frac{\text{mg}\cdot\text{mole NO}}{\text{g}}\right)^{-1}$		
T(°K)	θ	α_1	α_2	α_2/α_1
299	0.181	29.4	78.3	2.66
333	0.133	39.9	68.4	1.71
373	0.117	48.4	36.7	0.76
413	0.0769	55.2	31.4	0.57

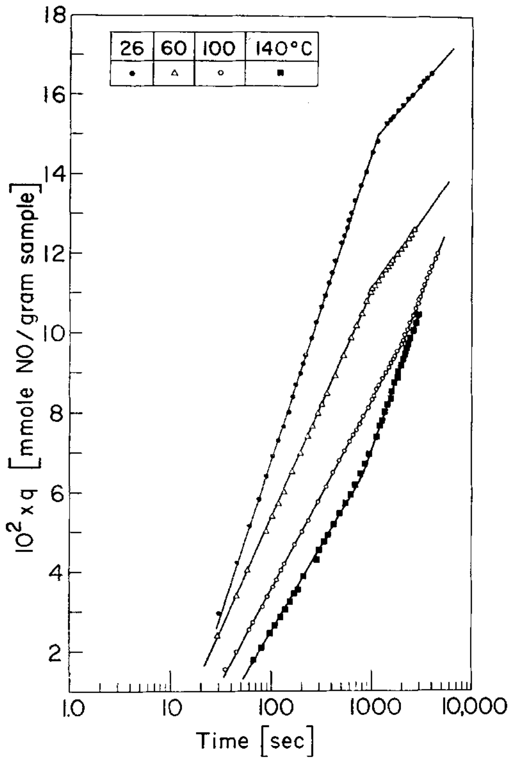

FIG. 3. Elovich plots for NO adsorption on supported copper oxide (SC1) in integral form.

Owing to the slow reoxidation mentioned above, the rate of NO adsorption on Cu_2O cannot be isolated: the oxidation weight gain is superimposed onto that associated with the adsorption and the rate data do not yield linear Elovich plots. However, a comparison of the combined rates of adsorption and oxidation on the reduced sample (Cu_2O) with the adsorption rate on cupric oxide reveals an interesting experimental fact. Data in Table 3 demonstrate that at temperatures below 100°C the rate of adsorption on the oxidized cupric oxide exceeds the combined weight gain of oxidation and adsorption for the reduced sample. Thus, contrary to the behavior observed previously on chromium (*1*) and iron (*2*) oxides, the adsorption rate on reduced copper oxide is slower than that on the oxidized samples. Only at 140°C (413°K) does the rate of oxidation of the cuprous ions overtake to diminished rate of adsorption on cupric oxide.

TABLE 3
WEIGHT GAIN AS A FUNCTION OF TIME ON OXIDIZED AND REDUCED SC1 (mg NO/g)

	Oxidized sample (CuO)			Reduced sample (Cu_2O)		
T (°K)	(sec): 1000	1800	3600	1000	1800	3600
299	4.36	4.68	4.93	1.53	1.77	2.08
333	3.33	3.61	3.92	1.56	1.86	2.28
373	2.50	3.01	3.42	1.26	1.62	2.28
413	2.13	2.70	3.36	2.13	3.00	4.32

C. *The Relationship Between Chemisorbed NO and Surface Copper Atoms*

As in the case of supported iron oxide (*1*) and nickel oxide (*3*), the surface density of the Cu atoms in the SC1 sample was estimated by comparison with adsorption on pure CuO (SC3) and on the diluted supported catalyst. Table 4 summarizes these findings. On the diluted catalyst (SC2) all the Cu ions are assumed to be on the surface. In this case, the observed ratio of total number of Cu atoms to the maximum NO uptake is close to unity. On pure CuO the maximum NO uptake is 0.00815 mmole NO/g (0.00836 mmole NO/m^2 BET), or 5.04×10^{18} NO molecules/m^2 BET. The density of surface Cu atoms in monoclinic CuO is not known accurately and it is assumed in the first approximation that it is not too different from the averaged surface density of Ni atoms on the low index planes in NiO (*7*). Then, if a second assumption is made that the half-populated surface is the stable configuration (*8*) the measured limiting uptake of NO is fairly close to a 1:1 correspondence between chemisorbed NO molecules and surface Cu atoms.

Based on a 1:1 correspondence between NO uptake to surface Cu atoms, the proportion of Cu atoms exposed on the surface in sample SC1 is ~60%. As noted above, this is also the upper limit of the oxidation of the Cu^+ by NO at room temperature. From the ratios of the uptakes on samples SC1 and pure CuO (SC3) it is deduced that out of the 168 m^2/g of surface area of

TABLE 4

COMPARISON OF Cu CONCENTRATION AND AMOUNT OF NO ADSORBED AT MONOLAYER COVERAGE

Catalyst designation	SC1	SC2	SC3
Wt % Cu	8.89	0.861	Pure CuO
Surface area (BET) (m^2/g)	167.90	170.68	0.97
Total amount of Cu (mg-atom Cu/g of catalyst)	1.40	0.1282	15.72
Monolayer coverage of NO (mmole NO/g)	0.84	0.12	0.00815
[Cu (total)(mg-atom)]/[NO (max)(mmole)]	1.67	1.07	1930

SC1 about 100 m^2 are covered with copper oxide.

D. *Comparison Between NO Chemisorption on Copper Oxide and Copper Aluminate*

A series of papers by Wolberg and coworkers (*9*) has been published to demonstrate by various physical techniques the formation of surface copper aluminates on the surface of alumina-supported copper oxide catalysts, even after calcination at relatively low temperatures of the order of 300°C, provided a proper combination of Cu concentration and Al_2O_3 surface area exists. In order to establish whether our supported catalyst behaved with respect to NO chemisorption in a manner similar to copper aluminate, we have measured NO chemisorption isotherms and rates on pure $CuAl_2O_4$.

Copper aluminate was prepared in the same manner as in Ref. (9a) according to the method of Holgersson (*10*) and verified to be pure $CuAl_2O_4$ by X-ray diffraction. Figure 4 shows the comparison of the NO uptake per unit area of CuO on a Al_2O_3 support and pure $CuAl_2O_4$. The square point on the lower line represents the uptake on unsupported CuO. As shown in Fig. 4, the equilibrium uptake on $CuAl_2O_4$ is somewhat higher than on CuO, although one would expect a lower surface population of Cu atoms. It means that some of the surface Al atoms in the $CuAl_2O_4$ chemisorb NO; it is conceivable that Al atoms in $CuAl_2O_4$ chemisorb NO to a larger extent than those in Al_2O_3. The NO adsorption on the alumina support for supported copper oxide (SC1) sample is only ~3% at 26°C and insignificant at higher temperatures. On the $CuAl_2O_4$ about 25% of total NO chemisorbed at 26°C is removed by pumping on the sample at room temperature and the balance by heating the sample at high temperatures. The reversible NO adsorption could be due to the weakly held NO molecules by surface Al atoms in the $CuAl_2O_4$ sample.

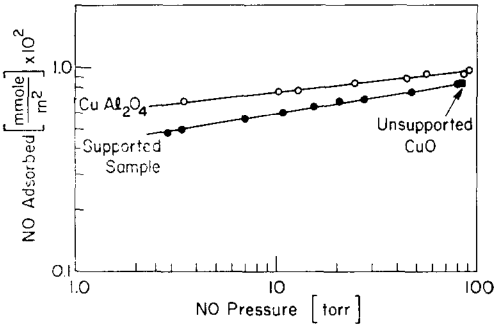

FIG. 4. Adsorption isotherm for NO on $CuAl_2O_4$ and supported copper oxide (SC1) at 26°C. (On the supported sample the ordinate refers to 1 m^2 of CuO area only.)

The important difference between the NO chemisorption on supported copper oxide and that on $CuAl_2O_4$ is in the rate of chemisorption and the shape of the Elovich plots as shown in Fig. 5. The chemisorption rate on the $CuAl_2O_4$ is still much slower than the slow rate on supported CuO, at least in the initial stages of the chemisorption process. We have to conclude, therefore, that with respect to its chemisorption characteristics copper ions deposited on an alumina surface under the specific conditions of our samples and calcined at 600°C do not behave as bulk $CuAl_2O_4$.

E. *Concluding Remarks*

Supported copper oxide behaves differently, in NO chemisorption, from the other

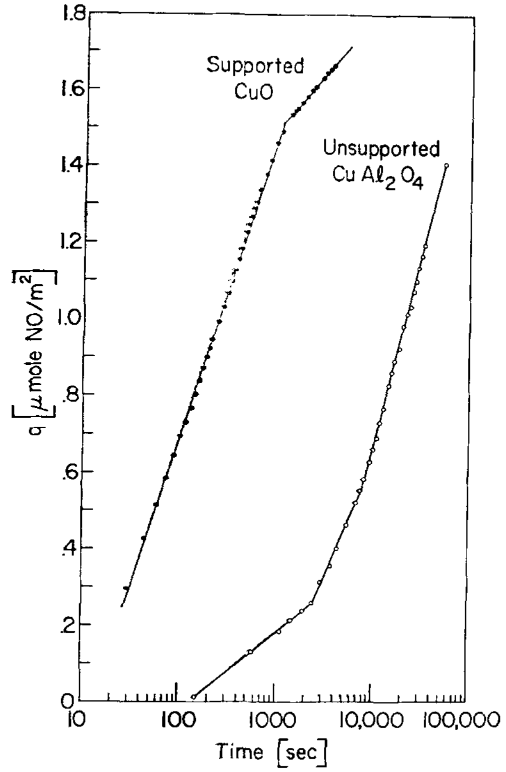

FIG. 5. Elovich plot for NO adsorption on supported copper oxide (SC1) and $CuAl_2O_4$ at 26°C in integral form. (On the supported sample the ordinate refers to 1 m^2 of CuO area only.)

previously investigated oxides of chromium (*1*), iron (*2*), and nickel (*3*).

First, the oxidized cupric surface ions chemisorb nitric oxide faster than the cuprous ions. It is quite possible that the cuprous ions do not chemisorb NO at all and the NO chemisorption on a given copper ion occurs only after its oxidation to the cupric state. There exists an exact analogy to this phenomenon in the chemistry of nitrosyl complexes (*11*): in general, solutions of cupric salts do absorb nitric oxide, while solutions of cuprous salts do not. Coordination of the nitric oxide molecule, required both in complex formation and in chemisorption, involves the transfer of the anti-bonding electron of the NO to an unpaired *d*-orbital of the coordinating ion. In Cu^{2+} ions (d^9) such an unpaired orbital is available; in Cu^+ (d^{10}) it is not. This assumption will be verified in the future by the study of NO chemisorption on zinc oxide where the Zn^{2+} ions have a (d^{10}) configuration. The adsorption of NO on diamagnetic adsorbents, such as ZnO takes place without electron pairing and therefore is observable by EPR. Such chemisorption was found to take place only on a minor part of the ZnO surface (*12*, *13*).

Second, on supported copper oxide the parallelism between the chemisorption rate and the relative activity in the NO–CO reaction observed on the other transition metal oxides (*3*) has broken down. The values of α_1 in Table 2, multiplied by a factor of 100 for conversion to units of $(\text{mmole NO/m}^2)^{-1}$ range from 3000 at 299°K to 5500 at 413°K. This is considerably higher than the α_1 values for the other supported catalysts which fall in the range 750 at 299°K to 4800 at 413°K. As the rate of chemisorption is inversely proportional to α, a slower rate is observed for supported copper oxide than for the other supported transition metal oxides. On the other hand, in the activity series for the NO–CO reaction (*14*), supported copper oxide is among the more active catalysts. A more detailed study of the NO–CO reaction mechanism on copper oxide is warranted to elucidate the rate determining step before the reason for this divergence can be pinpointed.

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