

Adsorption and Reduction of NO on Tin(IV) Oxide Catalysts

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Rates for NO chemisorption were measured on different samples of SnO₂ in the temperature range 25–150°C. Kinetic measurements revealed that the extent and the rate of NO adsorption on different surfaces increase in the order SnO_{2(oxidized)} ≪ SnO_{2(activated)} < SnO_{2(reduced)}. It was found that preadsorbed NO promotes the adsorption of CO, which was attributed to the formation of a surface isocyanate complex. Electrical conductivity measurements during NO adsorption revealed that both negatively and positively adsorbed species are present on activated surfaces.

The catalytic reduction of NO with CO on SnO₂ proceeded with reproducible rates only above 360°C. The reaction was of zero order with respect to CO and first order with respect to NO. The value of the activation energy is 36.6 kcal/mole. It was found that the catalytic reaction takes place on a weakly reduced surface. It is postulated that the reduced centers play an important role in the activation of NO, and NO dissociates upon adsorption. A possible mechanism of the catalytic reduction of NO is discussed.

INTRODUCTION

Although studies of the catalytic chemistry of NO have multiplied considerably in recent years, relatively little is known about the interaction of nitric oxide with metal oxide surfaces, and especially about the mechanism of the catalytic reactions between nitric oxide and different fuels (1, 2). In the case of the NO–CO reaction the chromium-based catalysts (chromium(III) oxide, copper(II) chromite) were found to be among the most active substances. As it appeared (3) that the reduction and oxidation of chromium plays a significant role in the catalytic reduction of nitric oxide, our attention turned to catalyst systems in which the reduction and oxidation of chromium is especially favored. A prominent catalyst in this respect is tin(IV) oxide containing a small amount of chromium(III) oxide. Investiga-

tion of the properties of SnO₂–Cr₂O₃ catalysts revealed that during its incorporation into SnO₂ in air a part of the chromium is converted to a higher oxidation state and stabilized in the surface layer of the *n*-type SnO₂ (4–6). A noteworthy feature of chromium in the surface layer of SnO₂ is that after its reduction with fuels it can easily be reoxidized, even at low temperatures.

In a preliminary communication we showed that SnO₂ containing a small amount of Cr₂O₃ is a very active catalyst for the reduction of NO with CO, H₂, and C₂H₄, even at low temperature (7).

In the present paper we report on the interaction of NO with SnO₂ surfaces and the reduction of NO with CO on this oxide. A subsequent paper will deal with the effects on these processes of using SnO₂ doped with chromium.

EXPERIMENTAL METHODS

Materials

SnO₂ was obtained by the action of HNO₃ on metallic Sn. It was dried at 120°C, and heated at 350°C for 3 hr and at 500°C for 5 hr. Final sintering was performed at 900°C for 5 hr in air. The surface area of the SnO₂ sample used was 5.8 m²/g. Nitric oxide (Matheson Ltd.) was of commercial purity (99%). It was purified by bulb-to-bulb distillation before use. The mass spectrum did not show the presence of NO₂ or N₂O₃. Carbon monoxide was prepared in the laboratory by reacting formic acid with sulphuric acid at 83°C.

For the catalytic studies, small pellets (1.5 mm in diameter and 1.5 mm long) were made. A fixed amount of catalyst (1.5 g, 8–10 small pellets) was used in every experiment.

Three different samples of catalyst have been used: (i) SnO₂ activated in vacuum at 400°C for 60 min, (ii) SnO₂ partially reduced with CO at 400°C for 60 min, (iii) SnO₂ oxidized with O₂ at 200°C for 60 min.

Apparatus

For the kinetic investigations a closed circulation system (volume 277 ml) was used. The reaction was followed by measuring the pressure of the reacting gases. For analysis of the reaction products an A.E.I. MS-10 mass spectrometer was connected to the reactor.

Conductivity measurements during adsorption and catalytic reaction were performed in the same reactor, using pellets 8 mm in diameter and 6–7 mm long. An ac bridge was used for these measurements. Specific surface areas were calculated from the adsorption of nitrogen at liquid nitrogen temperature.

Adsorption measurements were carried out in a Sartorius microbalance.

RESULTS

1. Adsorption of NO

A characteristic feature of the adsorption of NO on diamagnetic oxides is its extreme slowness. On aluminium oxides, for instance, 100 days are required to achieve an adsorption equilibrium (8, 9). In spite of the low heat of adsorption, Solbakken and Reyerson (8) came to the conclusion that the adsorption of NO on Al₂O₃ is a chemisorption process. Magnetic data showed that NO loses its paramagnetism when adsorbed; its odd electron is thus paired with an electron from the alumina gel surface. The adsorption of NO on transition metal oxides (Cr₂O₃, NiO, and CuO) has been studied recently by Shelef *et al.* (10–13).

a. Kinetics of adsorption. The primary aim of our adsorption studies was to compare the rate of adsorption of NO on different SnO₂ surfaces.

The adsorption of NO on SnO₂ is very slow, in spite of the fact that there is no experimental evidence for a substantial energy of activation. It may be concluded that the adsorption is associated with a very small preexponential factor.

Reversible adsorption was observed only on an oxidized surface. On an activated surface the adsorption was partly irreversible. In the case of the reduced surface the extent of the irreversibility (i.e., the relative amount of NO which, according to gravimetric measurements, is not desorbed at the same temperature) was higher. On an activated surface at adsorption equilibrium, at 105°C, after 2 hr of evacuation, 25% of the adsorbed NO remained on the surface. On a reduced surface this value was 45%.

The reversibly adsorbed fraction of NO on all three surfaces *desorbed as NO at 25–50°C*. Above 100°C the desorbing gases from the activated surface contained N₂ and N₂O, too. In the case of reduced

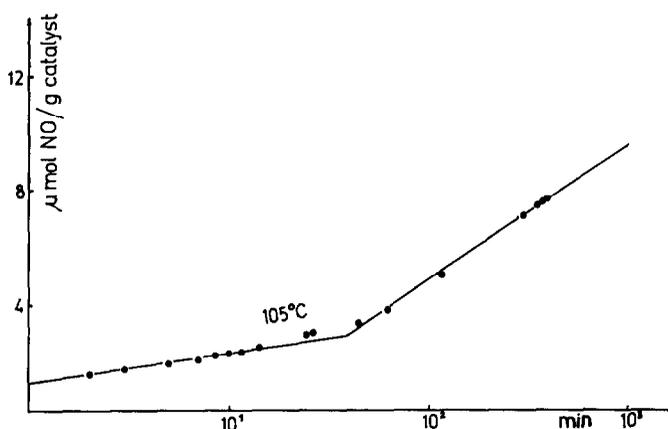


FIG. 1. Elovich plots in integrated form for NO adsorption on activated SnO_2 at 105°C and 10 Torr.

surface the amount of N_2O was smaller, whereas that of the N_2 was larger.

The chemisorption kinetics of NO were followed at 10 Torr at 25 – 150°C . The experimental results were evaluated with the integrated form of the Elovich equation

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

where $t_0 = 1/\alpha$ is an integration constant. Since $t_0 \ll t$, the above equation can be reduced to

$$q = (2.3/\alpha) \log t - (2.3/\alpha) \log t_0.$$

The Elovich plots consist of two linear segments with a distinct break between them (Fig. 1). A possible explanation of the break is that two distinct populations of adsorption sites exist on the surface.

The characteristic data of these plots are given in Table 1. The instantaneous adsorption of NO increases with the temperature. α_1 decreases rapidly, and α_2 slightly with T ; accordingly, the temperature coefficient of the adsorption is positive.

On partially reduced SnO_2 the instantaneous uptake of NO was markedly larger than that on an unreduced sample, and also increased with increase of the temperature. The Elovich plots were of the same character as in the case of activated SnO_2 . The coefficient α_1 was much smaller than that on activated SnO_2 , indicating that the rate of adsorption of NO was higher. Its value similarly decreased with increase of the temperature. No significant difference was found between the values of

TABLE 1
Characteristic Data of Elovich Equation

T ($^\circ\text{C}$)	Activated SnO_2				Reduced SnO_2			
	q_0^a ($\mu\text{mole/g}$)	α_1 [$\mu\text{mole/g}$] $^{-1}$	α_2	θ	q_0 ($\mu\text{mole/g}$)	α_1 [$\mu\text{mole/g}$] $^{-1}$	α_2	θ
25	0.8	4.45	0.35	0.036	1.9	4.1	0.13	0.042
50	0.91	3.45	0.47	0.053	2.35	1.3	0.14	0.081
105	1	2.1	0.46	0.057	3.15	0.76	0.15	0.115
150	1.16	1.6	0.46	0.047				

* q_0 = the amount of instantaneous adsorption.

α_2 . Attempts were made to measure the adsorption of NO on an oxidized surface (SnO₂ treated with O₂ at 200°C for 60 min and the system then evacuated for 5 min and cooled down to the temperature of adsorption). The adsorption of NO on this surface was extremely slight and slow.

For comparison of the adsorption rates on different SnO₂ surfaces, Table 2 shows actual rates measured at a constant coverage, $\theta = 0.065$. Measurements were made to determine the degree of irreversibility of NO adsorption in the first and second stages of the Elovich plots. On activated surface at 105°C, 85% of the adsorbate before the break in the Elovich plots is strongly held on the surface, while in the second stage the corresponding value is less than 30%.

b. Coadsorption and promoted adsorption. The coadsorption of NO + CO has been studied at 100°C in the case of SnO₂ activated in vacuum at 400°C. Using a mixture of NO + CO(1:1), the extent of adsorption was ten times larger than the sum for the separately adsorbed gases. Preadsorbed nitric oxide was found to promote both the rate and the extent of CO adsorption (Fig. 2). The ratio of the adsorbed NO and CO promoted approaches unity, pointing to the existence of a surface complex apparently containing equal numbers of moles of NO and CO. However, when the adsorbed amount of NO exceeded a certain value (1.1 $\mu\text{mole/g}$, $\theta = 0.03$,

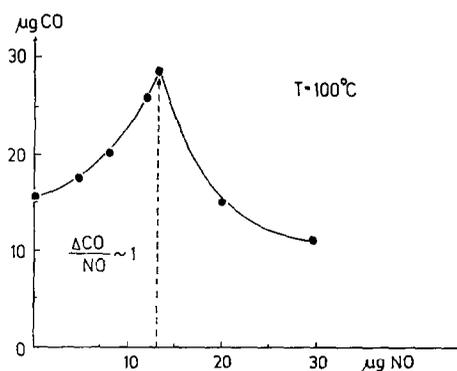


FIG. 2. The adsorption of CO on activated SnO₂ at 100°C as a function of the amount of preadsorbed NO.

in this case), the adsorption of CO decreased and finally the promotion changed into inhibition. This limiting value is very nearly the same as the amount of NO strongly adsorbed under similar experimental conditions. During the study of coadsorption and promoted adsorption at 100°C we did not detect significant quantities of CO₂ and other reaction products by mass spectrometric analysis. It is important to note that (i) adsorbed oxygen does not promote the adsorption of CO even on activated surface, (ii) preadsorbed CO does not enhance the adsorption of NO, and (iii) no promoted adsorption of CO occurred at 100°C, on oxidized surfaces.

2. Electrical Conductivity Measurements during the Adsorption of NO and CO

Some electrical resistivity measurements have been carried out during the adsorption of NO in order to characterize the nature of the electronic interaction between NO and *n*-type. SnO₂. The low ionization potential of NO, 9.5 V, makes possible the conversion of the nitric oxide molecule to the nitrosonium ion, NO⁺. NO can also easily take up an electron to be converted to a nitrosyl ion NO⁻. The lower limit to the electron affinity of gaseous NO is 0.65 eV (14). Figure 3 shows that the adsorption of NO increases the electrical resistivity of acti-

TABLE 2
Rates of NO Adsorption on SnO₂ Samples at $\theta = 0.065$

<i>T</i> (°C)	Oxidized ($\mu\text{mole/g}$ min)	Activated ($\mu\text{mole/g}$ min)	Reduced ($\mu\text{mole/g}$ min)
25		0.0516	0.0036
50		0.266	0.35
100	0.0070	0.730	3.28
150		1.300	

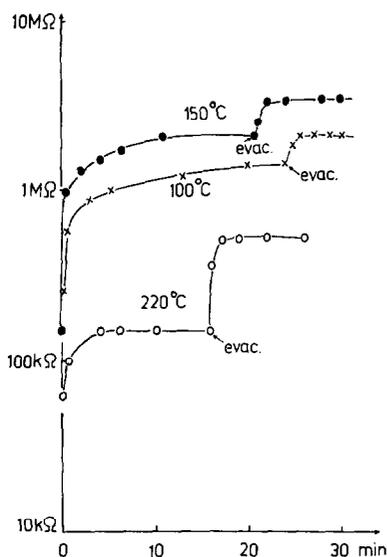


FIG. 3. The effect of NO and subsequent evacuation on the electrical resistivity of activated SnO_2 at different temperatures.

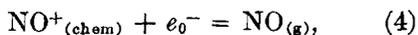
vated SnO_2 , which can be explained by the formation of negatively charged adsorbed species, NO^- and/or O^- , according to the equations



On evacuation of the NO from the reaction cell at the same temperature the electrical resistivity of the SnO_2 further increased to a small extent. This behavior indicates that, besides the above modes of adsorption, a part of the NO is chemisorbed by giving its unpaired electron to the oxide surface forming an apparently positively chemisorbed ion



This kind of NO adsorption partly compensated the result of the electron acceptor adsorptions [Eqs. (1) and (2)]. This adsorption is much weaker than the former ones, so that on evacuation of the sample NO from NO^+ desorbs from the surface



and as a result the electric resistivity of

SnO_2 increases. Qualitatively the same behavior was found at higher temperatures, up to 300°C . Above 300°C the formation of $\text{NO}^+_{(\text{chem})}$, if any, was not indicated by electrical conductivity measurements.

When NO was admitted to the catalyst in doses (25 Torr at a time), the effect of the second dose differed from that of the first. The extent of the first resistivity increase was smaller than in the case of the first NO dose, whereas that of second one was larger. On admission of the third dose the resistivity of the sample first decreased. On evacuation, however, the resistivity became higher than it had been before the third dose, indicating that both types of chemisorption processes had occurred on admission of NO, but that the effect of NO^+ formation exceeded that due to NO^- and O^- . After a further dose the resistivity of the sample again decreased, but on pumping off the gases the resistivity of the SnO_2 scarcely exceeded the value measured before this dose. It seems very likely that here the formation of negatively charged adsorbed species was very low compared to the previous cases and to the formation of NO^+ (Fig. 4).

This series of experiments convincingly shows that the activated tin dioxide surface has only a limited number of active sites available for the formation of negatively charged adsorbed species. When SnO_2 was not activated at 400°C in vacuum, but merely evacuated at the adsorption temperature (25 – 150°C), its resistivity decreased to only a small extent on introduction of NO. From this observation it can be inferred that SnO_2 is partially reduced during the activation process and that the reduced centers are responsible for the formation of NO^- and/or O^- .

Some preliminary mass-spectrometric analyses have been conducted on the composition of the gases desorbed from activated SnO_2 pellets. In this case NO was adsorbed on SnO_2 at 100°C for 60 min and the gaseous NO and the weakly held NO

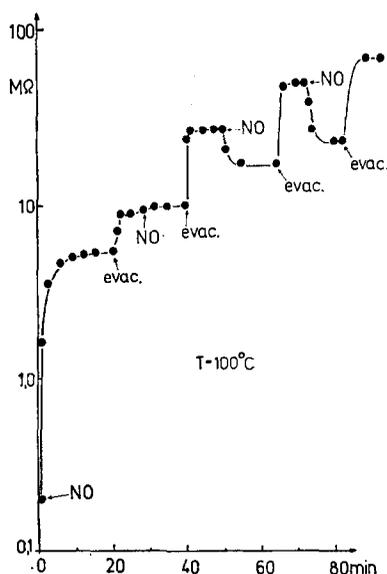


Fig. 4. The effect of NO doses (25 Torr) and subsequent evacuations on the electrical resistivity of activated SnO₂ at 100°C.

was pumped off for 5 min, and the sample was then kept at the same temperature for 60 min. In the gases desorbing at 100° we found NO (30%), N₂ (40%), and N₂O (28%). On heating the sample in vacuum to 180°C the desorption products contained only NO (80%) and N₂ (20%), whereas at 240°C it consisted of NO (36%), N₂ (53%), and O₂ (11%). On further heating of the sample to 320°C and then to 360°C only the partial pressures of N₂ and O₂ were increased. The molar ratio of N₂ and O₂ was 3 at 320°C and 1 at 360°C.

From these results it may be inferred that a part of the NO is adsorbed dissociatively on the activated surface, the extent of dissociation increasing with the temperature. Although the species most strongly held on activated SnO₂ is oxygen, very probably in the form of O⁻ ions, on the basis of these experiments the possibility cannot be excluded that the transient formation of NO⁻ ions also contributes to the electrical resistivity increase of SnO₂.

When a 1:1 mixture of NO + CO was admitted to the activated sample at 100°C, the electrical resistivity again in-

creased, and to a somewhat larger extent than in the case of NO, in spite of the fact that CO alone decreased the resistivity of SnO₂.



On evacuation the resistivity further increased. This is shown in Fig. 5. In the range 150–250°C the situation was somewhat different; the resistivity first increased, and then decreased, slowly approaching a steady-state value. Above 250°C the initial resistivity increase was not exhibited. In the temperature range of the catalytic reaction, 390–440°C, the electrical resistivity of SnO₂ decreased by one order of magnitude, and remained at this level until the very end of the catalytic reaction. The same behavior was observed with a slight excess of NO (NO:CO mole ratio 2.5:1). This indicates that at this temperature the reducing effect of CO is dominant and the catalyst is in a partially reduced state in the course of the catalytic reduction. The same types of resistivity vs time curves were obtained in the pres-

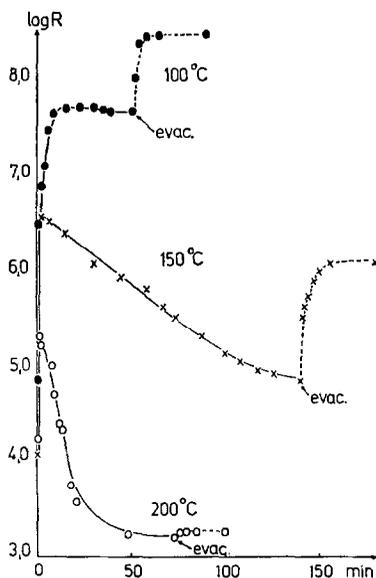


Fig. 5. The effect of NO + CO mixture (1:1) on the electrical resistivity of activated SnO₂ at different temperatures.

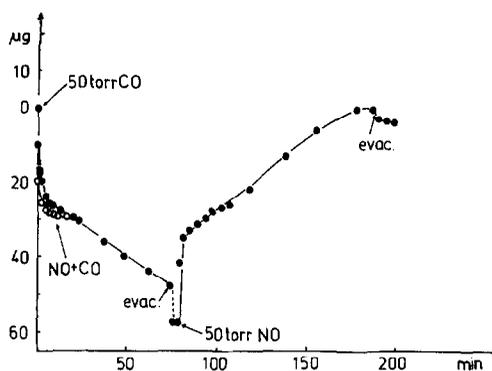


FIG. 6. The reduction and reoxidation of SnO_2 catalyst with CO, NO - CO (1:1) and NO at 418°C . The change in the weight of SnO_2 is plotted on the ordinate. The amount of SnO_2 was 0.4 g.

ence of CO alone, the initial resistivity increase not occurring.

3. Reduction and Reoxidation of Catalysts

Next a study was made of the reduction and reoxidation of catalyst samples at the temperatures of the catalytic reaction in the Sartorius microbalance. When CO was admitted to an activated sample at 400°C there was an initially rapid, and then a slower, weight decrease (Fig. 6). The rate of the initial stage was practically independent of temperature. The reoxidation of the reduced sample with NO also proceeds in two steps. It is to be noted that the oxidation of the reduced sample took place within a matter of moments on the action of an equivalent amount of oxygen, even if the temperature was decreased by almost 200°C . Using 1:1 mixture of NO and CO at the same temperature, the initial rapid weight decrease observed earlier on the introduction of CO alone was found here too, and its extent was practically the same as that in the absence of NO (Fig. 6). In the case of a CO excess, a further weight decrease (reduction) occurred with the consumption of the NO, while on the use of excess NO the catalyst weight slowly increased with the reaction of the CO until it attained the original weight of the starting material.

4. Kinetic Measurements

The reduction of NO by CO proceeded with reproducible rates and conversions in vacuum only above 360°C . After a slight initial decrease, the activity of the catalyst remained constant. The reduction of nitric oxide to nitrogen was practically complete. The transient formation of N_2O was observed during the experiments, its amount, however, always remaining below 2%. The rate of the reaction was not influenced by the reaction products (CO_2 , N_2) at 360 – 440°C .

The efficiency of SnO_2 was also tested at lower temperatures (150 – 360°C), where the initial rate and the conversion of the NO reduction depended sensitively on the pretreatment of the SnO_2 . Catalytic reaction on SnO_2 activated at 400°C in vacuum was observed even at 155°C . The conversion in the first run was 7.5%. In the second run, however, the SnO_2 was completely inactive. Similar behavior was experienced at higher temperatures up to 360°C , with the difference that the initial rate and the conversion of the reduction were higher.

When the SnO_2 was previously treated with CO at 400°C (reduced surface) the initial rate and the conversion of the catalytic reaction measured at 250 – 360°C were somewhat higher than for the activated catalysts. However, after treatment of the activated sample with NO or with O_2 for 1 hr at 155 – 360°C , the initial activity of the catalyst measured at the same temperature was significantly reduced.

Detailed kinetic measurements were carried out at 390 – 440°C with a stoichiometric mixture of the reacting gases. The reaction was of zero order with respect to CO, and first order with respect to NO (Fig. 7). The activation energy was 36.6 kcal/mole, and thus considerably larger than that of the CO-O_2 reaction (15). The same value was obtained with a CO-NO molar composition of 5:1. Kinetic data are given in Table 3.

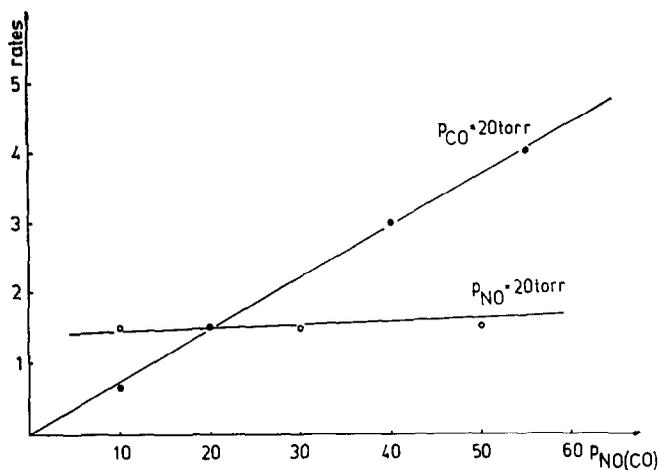
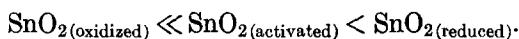


FIG. 7. The dependence of initial rates of NO-CO reaction on SnO₂ at 420°C as a function of partial pressure of NO and CO, respectively.

DISCUSSION

Adsorption measurements revealed that the extent and the rate of NO adsorption on different surfaces increase in the order



The irreversibility of NO adsorption also increases in this order. This indicates that the reduced centers of the SnO₂, very probably Sn³⁺ ions, play an important role in the adsorption and activation of the NO molecule. Mass-spectrometric analysis of the gases desorbed from the activated oxide indicated that NO dissociated upon adsorption, and as a result the catalyst surface became oxidized and inactivated.

From electrical resistivity measurements during the adsorption of NO it was concluded that both negatively and positively charged adsorbed species are present on the activated SnO₂ surface.

Since the formation of NO⁺ is accompanied by the strengthening of the N-O bond, while the transfer of an electron to the antibonding orbital of the NO leads to the greatest weakening of the bond, it seems plausible to assume that the oxidation of the catalyst surface occurs as a result of the transient formation and dissociation of the NO⁻ species.

It appears very likely that the presence of adsorbed nitrogen is responsible for the promoted adsorption of CO, possibly through the formation of a surface isocyanate complex



(M represents the active surface site, Sn³⁺ ion).

It is possible that the enhanced electrical resistivity of SnO₂ at 100°C in the presence of an NO-CO mixture, compared to the value obtained in NO or CO alone, is also a result of the formation of a surface isocyanate complex. Isocyanate species have

TABLE 3
Kinetic Data for the Catalytic
Reduction of NO^a

<i>T</i> (°C)	10 ⁻³ <i>k</i> _{spec} (min ⁻¹ m ⁻²)
398	0.67
405	1.1
420	2.4
420	2.4
430	3.4
440	4.5

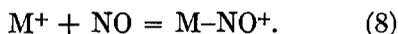
^a *E* = 36.6 kcal/mole; Frequency factor = 9.12 × 10⁸ min⁻¹ m⁻².

been detected by infrared spectroscopy during the reaction of NO with CO on the surface of noble metal catalysts (16) and also on supported CuO (17).

The fact that the extent of promoted adsorption exhibits a maximum as a function of the preadsorbed NO can be explained on the basis that only a limited number of active Sn^{3+} sites are available for the activation of the NO molecule and for the formation of adsorbed nitrogen. Measurements of the electrical resistivity of SnO_2 when NO was admitted in doses support this conclusion. The decrease of the extent of promoted adsorption at higher concentrations of adsorbed NO indicates that the gaseous NO combines with the adsorbed nitrogen



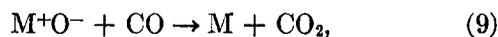
thereby reducing the possibility of formation of isocyanate species. The fact that at still higher concentrations of preadsorbed NO the promotion changed into inhibition means that in this case NO occupied the other adsorption sites, possibly the Sn^{4+} ions otherwise available for the adsorption of CO



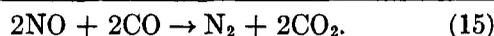
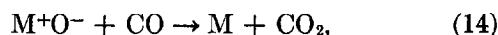
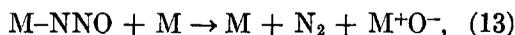
The observation that promoted adsorption of CO does not occur on an oxidized surface is in agreement with this picture.

From the study of the interaction of the reaction mixture with the catalyst during the catalytic process above 390°C by means of electrical conductivity and microgravimetric measurements, it appeared that the reduction of the SnO_2 surface with CO is much faster than the reoxidation of the reduced centers with NO. In agreement with this the oxidation of CO with NO takes place on the weakly reduced SnO_2 . Taking into account all our results and observations the following elementary steps are suggested for the reduction of NO with

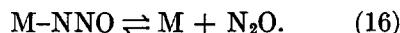
CO on SnO_2 :



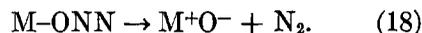
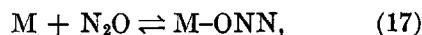
or



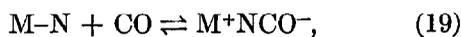
The transient appearance of N_2O in the gas phase is the result of the reaction



The decomposition of N_2O may occur in the reactions



An alternative to reactions (12)–(14) is that CO reacts with the adsorbed nitrogen atom and the reaction takes place through the formation of surface isocyanate complex



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