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Adsorption and Reduction of NO on Tin(IV) Oxide Doped with Chromium(III) Oxide

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Rates for NO chemisorption were measured on SnO_2 containing small amounts of Cr_2O_3. Evaluation of the NO chemisorption rate was done by the Elovich equation. Very large increases in the rate and amount of adsorbed NO were obtained by adding 1% Cr_2O_3 to SnO_2. It was found that preadsorbed NO promotes the adsorption of CO. Analyses of the gas-phase during the adsorption and thermal desorption measurements indicated that the extent of the dissociative adsorption of NO was greatly enhanced by adding Cr_2O_3 to SnO_2. The catalytic reduction of NO with CO on pure SnO_2 proceeded with reproducible rates and complete conversion only above 360°C. Catalytic reaction was detected below 200°C as well. The conversion of NO, however, was much less and the surface very soon became poisoned by CO. A marked increase in the efficiency of the catalyst was experienced when a small amount of Cr_2O_3 was incorporated into the SnO_2. The reduction of NO with CO occurred with a complete conversion and well-measurable rates at 150–220°C. CO exerted no poisoning effect at all. The high activity of SnO_2 containing Cr_2O_3 is attributed to the chromium ions located in the surface layer of SnO_2, which can easily be oxidized by NO and rapidly reduced by CO. A possible mechanism of the catalytic reduction of NO is discussed.

INTRODUCTION

Within a program for the development of an effective nonmetallic catalyst for the low-temperature reduction of NO pollutant, we have recently studied the interaction of NO with SnO_2 surfaces and the reduction of NO with CO on this oxide (*1*, *2*). Electric measurements during the adsorption of NO indicated that both negatively and positively charged adsorbed species are present on the activated SnO_2 surface. It was assumed that the transient formation and dissociation of the NO^- species are important for the catalytic reaction. SnO_2 catalyzed the NO + CO reaction at as low as 155°C. It lost its catalytic activity, however, very soon. Reproducible rates and complete conversion were obtained only above 360°C.

The adsorption and reduction of NO over SnO_2 has been recently investigated by other workers (*3*–*7*). The catalytic behavior of pure SnO_2 and the simultaneous formation of positively and negatively charged surface species during the adsorption of NO have been confirmed.

In the present paper, which is a direct continuation of our previous work, we report on some additional measurements with SnO_2 and deal with the effects of Cr_2O_3 additives on the adsorptive and catalytic properties of SnO_2. Incorporation of chromium into the surface layer of SnO_2 basically influences the surface properties of the SnO_2 (*8*, *9*) and results in a very effective catalyst for the low-temperature reduction of NO.

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EXPERIMENTAL METHODS

Materials. SnO_2 was obtained by the action of HNO_3 on metallic Sn. It was dried at 120°C, and heated at 350°C for 3 hr and at 500°C for 5 hr. The doping of the SnO_2 with Cr_2O_3 was effected in the following way: Cr_2O_3 was added to an aqueous suspension of SnO_2, and after a sufficiently long period of stirring, the homogeneous suspension was dried and heated at 350°C for 5 hr. Final sintering was done at 900°C for 5 hr in air. This preparation resulted in a catalyst containing higher-valence chromium ions stabilized in the surface layer of SnO_2. A fixed amount of catalyst (1.5 g, 8–10 small pellets) was used in every experiment. Three different samples of catalyst were employed: (i) catalyst activated in vacuum at 400°C for 60 min, (ii) catalyst partially reduced with CO at 400°C for 60 min, and (iii) catalyst oxidized with O_2 at 200°C for 60 min.

Nitric oxide (Matheson Ltd.) was of commercial purity (99%); it was purified by bulb-to-bulb distillation before use. Carbon monoxide was prepared in the laboratory by reacting formic acid with sulfuric acid at 83°C.

Apparatus. For the kinetic investigation a closed circulation system combined with an MS 10 mass spectrometer was applied. The volume of the reactor was 232 ml. A stoichiometric mixture of the reacting gases was used.

Adsorption measurements were carried out in a Sartorius microbalance.

The active oxygen content of the catalyst was determined by the Bunsen method (*8*, *9*). The degree of reduction of partially reduced SnO_2 catalysts was determined by dissolving 1- to 2-g samples in 20 ml of gently refluxing HBr solution (*10*). After dissolution, the solution was cooled and titrated with standard iodide–iodate solution.

Specific surface areas were calculated from the adsorption of nitrogen at liquid nitrogen temperature.

RESULTS

Kinetics of Adsorption

First the chemisorption kinetics of NO were followed on SnO_2 containing different amounts of Cr_2O_3. Before the adsorption the samples were evacuated at 400°C for 1 hr. The adsorption of NO was practically the same up to 0.1% Cr_2O_3 content. The extent of initial adsorption and rate of adsorption were somewhat higher on SnO_2 + 0.5% Cr_2O_3. More significant ad-

TABLE 1

Characteristic Data for NO Adsorption

Catalysts	Activated				Oxidized		
	T (°C)	q_0[a] (μmol/g)	α $(\mu mol/g)^{-1}$	Irreversibility (%)	q_0 (μmol/g)	α $(\mu mol/g)^{-1}$	Irreversibility (%)
SnO_2	25	0.80	4.4	31.5			
	50	0.91	3.4	25.0			
	105	1.00	2.1	18.2	0.32	11.5	0
SnO_2 + 0.5% Cr_2O_3	100	1.25	1.7	33.5			
SnO_2 + 1% Cr_2O_3	25	3.80	0.5	65.4			
	50	5.10	0.48	71.0			
	100	5.12	0.47	77.2	2.90	4.14	25.7

[a] q_0 = the amount of instantaneous adsorption.

sorptions and rates were observed for samples containing 1% Cr_2O_3. The initial uptake of NO was five times larger than on activated SnO_2.

The adsorption was partly irreversible on all Cr_2O_3-containing samples. The extent of irreversibility (i.e., the relative amount of NO which, according to gravimetric measurement, is not desorbed at the same temperature) was higher than on activated SnO_2 and increased with the Cr_2O_3 content and with the temperature (Table 1). The reversibly adsorbed fraction of NO desorbed as NO at 25–50°C. Above 100°C the gases desorbing from $SnO_2+1\%$ Cr_2O_3 contained N_2 and N_2O. Some adsorption curves are shown in Fig. 1.

The adsorption rates 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 $t_0 = 0.7$ min. The Elovich plots consisted of one linear section (Fig. 2). The coefficient α decreased with the temperature, but the extent of the decrease was smaller than on SnO_2. With the rise of the temperature, the extents of both the initial fast adsorption and the irreversibility of the NO adsorption increased slightly.

In the case of pure SnO_2 the chemisorption of NO depended on the pretreatment of the sample. A higher rate was obtained when the sample had previously been evacuated or partially reduced at 400°C.

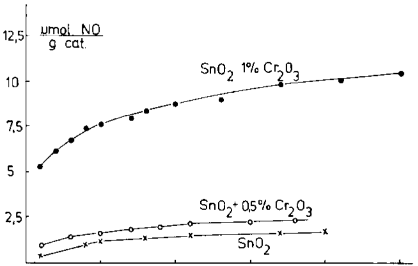

FIG. 1. Adsorption of NO on SnO_2 containing different amounts of Cr_2O_3 at 100°C and 10 Torr.

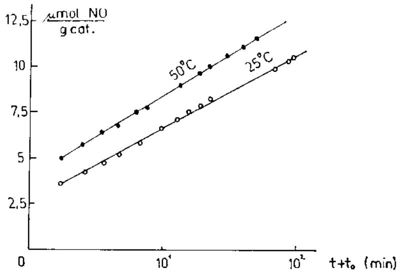

FIG. 2. Elovich plots in integrated form for NO adsorption on activated $SnO_2 + 1\%$ Cr_2O_3 at 10 Torr.

In the present case the reduction of $SnO_2 + 1\%$ Cr_2O_3 with CO at 250°C increased the adsorption of NO only a little. In contrast, on an oxidized surface both the initial uptake and the rate of adsorption decreased. The data for the chemisorption of NO are collected in Table 1. For comparison the data obtained for activated SnO_2 are also shown.

Coadsorption of NO + CO

The adsorption of NO + CO was studied at 25°C on $SnO_2 + 1\%$ Cr_2O_3 activated in vacuum at 400°C. The extent of gas uptake from the NO + CO mixture 1:1 was 1.5 times larger than the sum for the separately adsorbed gases. It turned out that the preadsorbed NO promoted the subsequent adsorption of CO; it increased both the initial uptake and the rate of chemisorption of CO. Similar behavior was found earlier on pure SnO_2, where it was attributed to the formation of a surface complex between NO and CO (*1*).

Thermal Desorption

To learn more about the interaction of NO with the catalyst surfaces, some measurements were made on the thermal desorption of NO from activated SnO_2 and $SnO_2 + 1\%$ Cr_2O_3 surfaces. NO (10 Torr) was adsorbed at different temperatures for 30 min. The sample was cooled to room temperature, then evacuated for

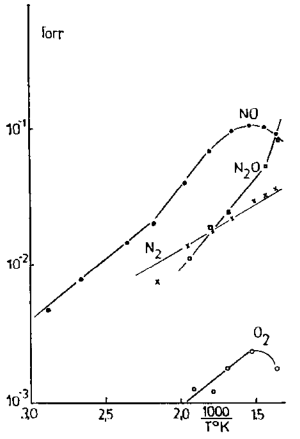

FIG. 3. Thermal desorption of gases from activated SnO_2 after the adsorption of 10 Torr NO at 25°C for 30 min. The gases were pumped off at 25°C for 30 min. Heating rate was 6°C/min.

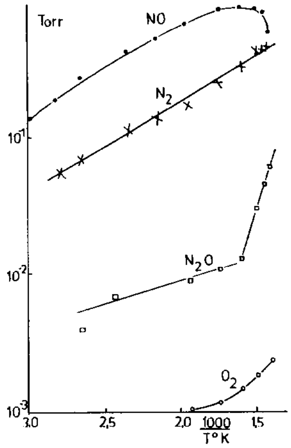

FIG. 4. Thermal desorption of gases from activated SnO_2 + 1% Cr_2O_3 after the adsorption of 10 Torr NO at 25°C for 30 min. The gases were pumped off at 25°C for 30 min.

30 min and heated at a rate of 6°C/min. The gases desorbed were analyzed by mass spectrometry.

In the case of pure SnO_2 the composition of the gas phase changed only above 200°C, when small amounts of N_2O, N_2, and O_2 appeared. On SnO_2 + 1% Cr_2O_3 this phenomenon was observed at lower temperatures. Analysis of the gas phase showed the dissociation of NO on SnO_2 + 1% Cr_2O_3 at 300°C to be four times higher than on pure SnO_2.

After adsorption at 25°C NO desorbed from both samples up to 370–390°C. N_2 appeared first at 185°C on SnO_2, and at 85°C on SnO_2 + 1% Cr_2O_3. The amounts of desorbed NO and N_2 were almost 10 times larger for SnO_2 + 1% Cr_2O_3. N_2O appeared at 240°C on SnO_2, and at 100°C on SnO_2 + 1% Cr_2O_3. A small amount of O_2 was detected in both cases, first at 250°C. Some results are shown in Figs. 3 and 4.

TABLE 2

Characteristic Data for Thermal Desorption of NO

Temperature of NO adsorption (°C)	Decomposition of NO during the adsorption (%)	Amount of desorbing gases (Torr)			Temperature of the onset of the desorption (°C)	
		NO	N_2	N_2O	N_2	N_2O
SnO_2						
25	0	1.0×10^{-1}	3.1×10^{-2}	5×10^{-2}	185	240
210	1.9	2.0×10^{-1}	1.0×10^{-1}	9×10^{-2}	190	155
300	2.2	2.5×10^{-1}	9.2×10^{-2}	2×10^{-2}	100	155
400	2.9	3.6×10^{-1}	3.2×10^{-1}	1×10^{-1}	100	120
SnO_2 + Cr_2O_3						
25	0	8.1×10^{-1}	4.3×10^{-1}	6.0×10^{-2}	85	100
210	6.9	1.2	7.0×10^{-1}	1.5×10^{-1}	95	95
300	11.7	1.2	4.5×10^{-1}	4.5×10^{-2}	85	90

A similar picture was observed when NO was adsorbed at a higher temperature, with the difference that as a result of the larger irreversible adsorption of NO, the amount of desorbing NO and N_2 were larger. Data concerning these measurements are collected in Table 2.

Study of the Catalytic Reaction between NO and CO

Whereas the reduction of NO with CO on pure SnO_2 occurs with a complete conversion above 360°C, on SnO_2 containing a small amount of Cr_2O_3 the reaction is complete at surprisingly low temperatures, 150–220°C. The reaction rate depends on the pretreatment of the catalysts; higher rates were measured on evacuated samples than on oxidized surfaces. As Fig. 5 shows, on activated $SnO_2 + 1\%$ Cr_2O_3 NO was reduced to N_2, but the transient formation of N_2O was also observed. The formation of N_2O was always larger at lower temperatures. The highest concentration of N_2O was detected at the beginning of the catalytic reaction; here almost 50% of the NO was transformed into N_2O. With the progress of the reaction its concentration decreased, and it disappeared before complete reduction of the NO. When CO was used in excess (NO:CO mole ratio of 1:2, at 210°C), no N_2O was detected by mass spectrometric analysis.

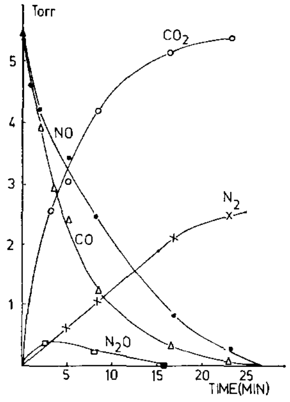

FIG. 5. Mass spectrometric analyses of NO–CO reactions over $SnO_2 + 1\%$ Cr_2O_3 at 170°C.

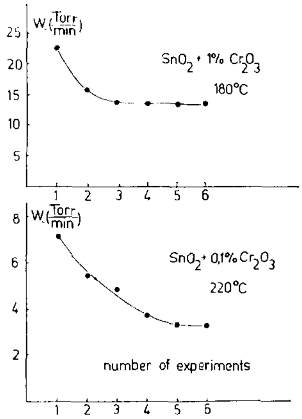

FIG. 6. The change in activity of $SnO_2 + 0.1\%$ Cr_2O_3 and $SnO_2 + 1\%$ Cr_2O_3. w_0 = initial rate of the reaction.

The change in activity of the catalysts was investigated at 210°C (0.1% Cr_2O_3) and at 180°C (1% Cr_2O_3). The activity of $SnO_2 + 1\%$ Cr_2O_3 (pretreated in vacuum at 400°C) changed only slightly after the second run. A somewhat larger activity change was observed on $SnO_2 + 0.1\%$ Cr_2O_3 (Fig. 6).

In view of the large promotor effect observed using as little as 0.1% Cr_2O_3, it seemed necessary to investigate more thoroughly the behavior of pure SnO_2 at lower temperatures too. It was found that the rate and the conversion of the NO reduction at 150–360°C depended sensitively on the pretreatment of the SnO_2. When SnO_2 was evacuated at 400°C for 60 min, the reaction at 155°C stopped at about 5% conversion. In the second run no reaction was observed at all. At 210°C the conversion of NO reduction was first 45%, but in the repeated experiment it was only 6.7%. The same behavior was experienced at 280°C. When SnO_2 had not been activated in vacuum at 400°C, no catalytic reaction was measurable in the low-temperature range 150–210°C. Some

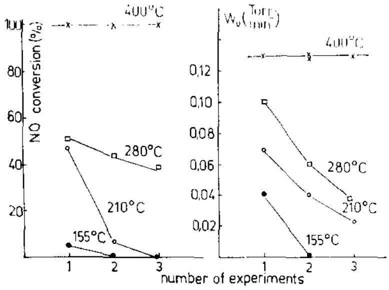

FIG. 7. The change in activity of SnO_2 at different temperatures. w_0 = initial rate of the reaction.

results of these experiments are shown in Fig. 7.

Since no such drastic activity decrease was experienced on SnO_2 containing Cr_2O_3, for an understanding of the catalytic behavior of the SnO_2–Cr_2O_3 system it was considered crucial to establish the reason for the great activity decrease of pure SnO_2.

In the interpretation of the catalytic behavior of pure SnO_2 we postulated that the reduced surface centers, very likely Sn^{3+} ions, play an important role in the adsorption and activation of NO (*1*). Accordingly, one of the possible reasons for the loss of catalytic activity of SnO_2 is that the NO oxidizes the reduced centers produced during the activation of SnO_2 at 400°C, and CO cannot reduce the reoxidized centers, Sn^{4+} ions, at such low temperatures. A detailed study of the reduction of SnO_2 with CO, however, showed that CO can reduce SnO_2 at as low as 180°C. It should be mentioned here that SnO_2 is a very efficient catalyst for the $O_2 + CO$ reaction at 180–250°C (*10, 11*). *Moreover, we found that the* $O_2 + CO$ *reaction occurred at the very same high rate on the* SnO_2 *which had become inactive in the* $NO + CO$ *reaction.*

Another possibility for the loss of catalytic activity of SnO_2 at low temperature is that the active sites are poisoned by the strong adsorption of reaction products or reactants. To clarify this point the SnO_2 was heated up at a constant heating rate after its catalytic activity had been exhausted at 210°C, and the desorbing products were analyzed. Before heating, the gaseous species were pumped off for 5 min at 210°C. The desorption spectrum is shown in Fig. 8.

The desorption products were carbon monoxide and carbon dioxide. Carbon monoxide desorbed continuously from 220°C up to 400°C. Carbon dioxide desorbed in two stages, at 220–300°C and 350–430°C. The amounts of CO and CO_2 desorbed were 1.9×10^{17} CO molecules/m^2 and 2.7×10^{17} CO_2 molecules/m^2. An important result was that no oxygen, nitrogen, or nitrogen oxides were found in the desorbing gases. When CO_2 was adsorbed on SnO_2 at 210°C for 60 min and evacuated for 5 min, CO_2 was not found during the thermal desorption up to 430°C. This indicates that CO_2 found in desorbing gases after the catalytic reaction was mainly the result of the reaction between the strongly adsorbed CO and SnO_2 surfaces. Further measurements showed that treating SnO_2 with CO_2, NO, or N_2O influenced the rate and conversion of NO reduction at 210°C only slightly. In contrast, treating the SnO_2 at 210°C with CO (10 Torr) markedly lowered its catalytic activity (Fig. 9). The inhibiting effect of CO was exhibited even after

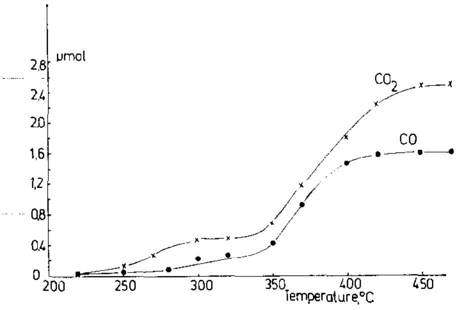

FIG. 8. The desorption spectrum of gases from SnO_2 after its catalytic activity had been lost at 210°C. The heating rate was 6°C/min. The amount of catalyst was 1 g.

adsorption for 5 min. When CO was adsorbed on SnO_2 for 30 min and then evacuated, practically no catalytic reaction between NO and CO was measurable on this sample at this temperature. After the treatment in vacuum at 400°C for 60 min the initial activity of SnO_2 was restored.

In view of these results, the same kinds of measurements were carried out on SnO_2 containing Cr_2O_3. In the case of $SnO_2 + 0.1\%$ Cr_2O_3 the preadsorbed CO also decreased the initial activity of the catalyst, but the catalyst remained in an active form and the conversion of NO reduction was always complete. In contrast to this, CO exerted no poisoning effect at all on the $SnO_2 + 1\%$ Cr_2O_3 catalyst.

Kinetic measurements were carried out in the temperature range 150–220°C. After steady-state activity was reached, the reaction was zero order with respect to CO and first order with respect to NO. The reproducibility of the rate constants in this stage was ±8.8%. The activation energy was considerably lower than that obtained for pure SnO_2 (36.6 kcal/mol), and it decreased with increase of the amount of Cr_2O_3 in the SnO_2. The catalytic performances of several different samples of appropriately prepared SnO_2 catalysts containing 1% Cr_2O_3 were practically the same. In the stage of steady-state activity the deviations of the rate constants determined on different samples from the average rate constant were less than ±40%. Kinetic data are given in Table 3.

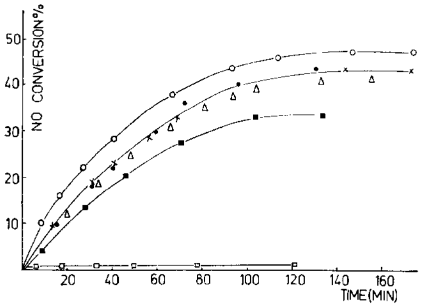

FIG. 9. The effect of treating the SnO_2 catalyst with different gases on the reduction of NO with CO at 210°C. The gases (10 Torr) were adsorbed before the catalytic reaction at 210°C for 30 min and evacuated for 10 min. (●), without gas adsorption; (○), NO; (×), N_2O; (△), CO_2; (□), CO; (■), CO (adsorption time, 5 min).

Some measurements were subsequently made concerning the effect of the preliminary heat treatment of $SnO_2 + 1\%$ Cr_2O_3 on its catalytic behavior. In our previous paper it was shown that the electric properties and the active oxygen content of Cr_2O_3-doped SnO_2 sensitively depend on the sintering temperature (*9*). The rate of the catalytic reaction of NO on $SnO_2 + 1\%$ Cr_2O_3 also varied with the heat treatment of the catalyst. The highest rate was obtained on the sample calcined at

TABLE 3

Kinetic Data for the Catalytic Reduction of NO[a]

Catalysts	Surface area (m^2/g)	Active oxygen content (%)	Temperature range (°C)	k_{spec} 210°C (min^{-1} m^{-2})	E (kcal/mol)	Frequency factor (min^{-1} m^{-2})
SnO_2	5.81	—	400–440	9.7×10^{-4}[b]	36.6 ± 3.6	9.1×10^{8}
$SnO_2 + 0.01\%$ Cr_2O_3	6.12	0.002	370–410	1.2×10^{-3}[b]	35.7 ± 3.5	6.8×10^{8}
$SnO_2 + 0.1\%$ Cr_2O_3	6.58	0.01	210–252	3.2×10^{-4}	21.9 ± 2.4	2.8×10^{6}
$SnO_2 + 0.5\%$ Cr_2O_3	8.84	0.043	200–245	4.4×10^{-4}	20.2 ± 2.1	3.2×10^{5}
$SnO_2 + 1\%$ Cr_2O_3	11.8	0.092	150–210	1.8×10^{-3}	18.2 ± 1.2	4.9×10^{5}

[a] The catalysts were sintered at 900°C in air.

[b] At 400°C.

700°C, on which the oxidation of chromium occurred to the greatest extent.

DISCUSSION

Before interpreting the large promotor effect of Cr_2O_3 additives and proposing an explanation for this, we shall deal briefly with two points: (i) with the pure SnO_2 catalyst, and (ii) with the physical–chemical properties of $SnO_2 + Cr_2O_3$.

(i) Adsorption measurements on SnO_2 samples revealed that the rate and the extent of NO adsorption as well as the dissociation of NO increased with the removal of the adsorbed oxygen and with the partial reduction of SnO_2 surface. From this it was inferred that the Sn^{3+} ions formed in the surface of SnO_2 play a dominant role in the adsorption and activation of the NO molecule.

The catalytic reduction of NO with CO on SnO_2 proceeded with reproducible rates and complete conversion only above 360°C. The activated SnO_2, however, catalyzed the reaction at much lower temperatures. The conversion of NO, however, was much less; the surface very soon became poisoned by CO in this temperature range, and as a result the rate and the conversion of NO reduction were decreased. From the study of the coadsorption of NO + CO on activated SnO_2 it was inferred that a surface complex, possibly isocyanate, was formed (*1*). The formation of this surface complex, however, cannot be responsible for the reaction inhibition, as the gases desorbing from the SnO_2 which had lost its activity included no nitrogen-containing compounds.

It seems very likely that CO adsorbs on the same sites as does NO, or more precisely on active sites (Sn^{3+} ions) on which the dissociative adsorption of NO, important for its catalytic reduction, occurs.

If we assume that during the activation (partial reduction) of SnO_2 only Sn^{3+} ions are formed [ESR measurements on evacuated SnO_2 in fact proved the presence of Sn^{3+} ions (*12, 13*)] and that this mild reduction is restricted only to the surface layers, from the oxygen deficiency the number of surface Sn^{3+} ions can be calculated. The oxygen deficiency of SnO_2 surface activated in vacuum at 400°C for 60 min was found to be 0.225 μmol/m^2 which is equivalent to 5.4×10^{17} Sn^{3+} ions/m^2. [This corresponds to a surface reduction of 2.4% provided that the oxygen availability on SnO_2 surface is 9.38 μmol (O_2)/m^2 (*14–16*).] The amount of adsorbed CO which completely stopped the catalytic reaction was calculated from the thermal desorption measurements performed after the ceasing of the catalytic reaction (Fig. 8). The value found (4.6×10^{17} molecules/m^2) is commensurate with the number of surface Sn^{3+} ions.[1]

We note here that our results and interpretation concerning the loss and decrease of the activity of SnO_2 at 210–360°C are in contrast to the recent view of Keyer *et al.* (*3*). They postulated that the adsorption of CO_2 and the reduction of SnO_2 with CO are responsible for the loss in activity of SnO_2. The fact that the catalytic activity of SnO_2 at 210°C can be restored by evacuation at 400°C seems to prove that at least at this temperature the activity decrease is primarily caused by the adsorption of CO. When SnO_2 was reduced previously at higher temperatures, above 400°C, then, in agreement with the results of Keyer *et al.*, the catalytic activity of this reduced sample at 210°C was significantly lowered. This treatment, however, in our case resulted in a deeper reduction (oxygen deficiency, 3.89 μmol/m^2; surface reduction, 41.5%) and possibly in the formation of SnO. This surface, the oxidation of which with NO is very slow at low temperatures, obviously cannot

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[1] It was assumed that the CO_2 desorbed is the result of the reaction of strongly adsorbed CO and surface oxygen of SnO_2.

be compared to the surface produced by adsorption of CO and by the catalytic reduction of NO + CO at 210°C.

It is interesting to mention that the extent of surface reduction of SnO_2 plays an important role in other catalytic reactions, namely, in the selective oxidation of propylene to benzene. The highest selectivity was obtained when the surface of SnO_2 was only partially reduced (*16*).

(ii) Study of the properties of a $SnO_2 + Cr_2O_3$ system sintered in air revealed that the incorporation of Cr_2O_3 into the *n*-type SnO_2 begins at 450°C and is accompanied by a decrease of the electric conductivity of SnO_2 (*9*).

The chromium ions incorporated into the surface layer of SnO_2 exhibit a very high reactivity; they can easily be oxidized to a higher valency state, while the higher-valence chromium can be rapidly reduced by different reducing agents and even by evacuation at 400°C (*9*). As a result of this high reactivity the $SnO_2 + Cr_2O_3$ samples sintered in air above 450°C contain a significant amount of excess oxygen, i.e., higher-valence chromium ions (Table 3).

The results presented showed that incorporation of a small amount of Cr_2O_3 into the surface layer of SnO_2 resulted in a very active catalyst for the reduction of NO with CO at low temperatures. The preparation of $SnO_2 + Cr_2O_3$ seems to be very important in producing a catalyst with high activity, as the coprecipitation of SnO_2 with Cr_2O_3 (Cr:Sn atomic ratio, 0.1:1) resulted in a deleterious effect on the catalytic activity of the SnO_2 (*6*).

The enhanced activity of SnO_2 containing chromium cannot be attributed to the change of the concentration of Sn^{3+} ions, as the large inhibiting effect of CO experienced on pure SnO_2 at the same temperature was not exhibited here. *This may indicate that the catalytic sites on $SnO_2 + Cr_2O_3$ catalyst are different from those on pure SnO_2.*

We suggest that the active catalytic sites on $SnO_2 + Cr_2O_3$ catalysts are the chromium ions located in the surface layer of the SnO_2. It seems very likely that the high reactivity of these chromium ions is responsible for the enhanced dissociation of NO observed above 200°C (Table 2) and for the outstanding catalytic effect of $SnO_2 + Cr_2O_3$ samples.

Provided that all the surface chromium in SnO_2 can be oxidized, the active oxygen content of the solid samples can be regarded as a measure of the active sites of the catalysts. In agreement with this, those samples possessed high catalytic activity where this surface oxidation had occurred to the greater extent. When the extent of the incorporation of Cr_2O_3 into the bulk was larger (sintering at 1100°C) or the incorporation of chromium (and its oxidation) was negligible (sintering at 350°C), the catalytic activity of the oxide mixtures was much less.

From the active oxygen content (higher-valence chromium) of the samples, the concentration of surface chromium can be calculated. Assuming that the oxidation of chromium occurs to oxidation state 5.5, similar to the case of chromium supported on alumina (*17*), we found that the $SnO_2 + 1\%\ Cr_2O_3$ (sintered at 900°C) contained 3.7×10^{18} surface chromium ions/m^2.

The number of surface chromium ions was also determined from the adsorption of NO at 25°C. Shelef and Kummer (*18*), investigating the adsorption of NO on supported transition metal ions, found that one surface metal ion adsorbs one NO. This correlation was used for the determination of the surface dispersion of transition metal ions. In the case of $SnO_2 + 1\%\ Cr_2O_3$ this method indicated that the number of surface chromium ions is 1.48×10^{18} ions/m^2.

We propose that the reduction of NO on $SnO_2 + Cr_2O_3$ catalysts involves the following elementary steps: (M denotes the tervalent chromium ions located in the surface layer of SnO_2.)

$$M^+O^- + CO \rightarrow M + CO_2 \quad (1)$$

$$M + NO \rightarrow M\text{-}NO \quad (2)$$

$$M\text{-}NO + M \rightarrow M\text{-}N + M^+O^- \quad (3)$$

$$M\text{-}N + NO \rightarrow M\text{-}NNO \quad (4)$$

$$M\text{-}NNO + M \rightarrow M + N_2 + M^+O^- \quad (5)$$

$$M^+O^- + CO \rightarrow M + CO_2 \quad (6)$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \quad (7)$$

The formation of N_2O was also observed during the reaction of $SnO_2 + Cr_2O_3$ catalysts, especially at lower temperatures. The source of N_2O is very probably the reaction

$$M\text{-}N\text{-}NO \rightarrow M + N_2O \quad (8)$$

which follows step (4). N_2O disappeared very quickly from the gas phase, however, in agreement with our experience that $SnO_2 + Cr_2O_3$ is a very effective catalyst for the decomposition of N_2O (*11*).

Further studies are required to decide whether formation of a surface complex, possibly isocyanate, plays a role in the reduction of NO with CO on $SnO_2 + Cr_2O_3$ catalysts:

$$M\text{-}N + CO \rightarrow M\text{-}NCO \quad (9)$$

$$M\text{-}NCO + NO \rightarrow M + N_2 + CO_2. \quad (10)$$

On the basis of the adsorption measurements on activated SnO_2, the formation of this surface complex has been assumed (*1*), but so far it has not been confirmed by infrared spectroscopy. Very recently, however, the formation of surface isocyanate was detected by infrared spectroscopy in a very similar system, on a reduced Al_2O_3/Cr_2O_3 catalyst (*19*). It formed with high intensity at the temperature of the catalytic reaction, and it reacted quickly with nitrogen oxides at 200°C.

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