

Temperature Programmed Desorption Study of the Interaction of CO₂ with a Co₃O₄ CO-Oxidation Catalyst

In previous work (1) it has been shown that in CO oxidation on Co₃O₄ at -80 to 150°C, the CO₂ formed inhibits the reaction by blocking the catalytically active surface sites. Poisoning is considered to be due to retention of CO₂ on the active sites in a chemisorbed form, with a surface carbonate species being formed at higher temperatures. A very strong poisoning effect is observed after preadsorption of CO₂. Similar general behavior has been reported by Rank and Teichner (2) and by Kondo, Uchijima and Yoneda (3) for CO oxidation on NiO.

Useful information on the forms of CO₂ adsorption on oxide surfaces and the temperature interval of their stability can be obtained by the method of temperature programmed desorption (TPD). In the present work this technique has been applied to study the forms of CO₂ adsorption on Co₃O₄.

The apparatus used was essentially the same as described previously (4, 5). It consisted basically of two parts, namely, an adsorption system in which adsorbed gas was measured volumetrically and a TPD system in which adsorbed gas was later desorbed in a helium carrier gas stream by programmed heating of the catalyst. The concentration of the desorbed carbon dioxide was measured and recorded by a thermal conductivity detector. The desorbed CO₂ was collected in a liquid nitrogen trap and its quantity again was measured.

Cobaltous-cobaltic oxide has been prepared by the thermal decomposition of Co(NO₃)₂·6H₂O (G.R.) in air at 400°C, and calcined for 15 hr at 620°C for stabilization of its surface area. The measurements were conducted on samples with

grain size 0.3-0.6 mm and a BET surface area of 1.17 m² g⁻¹.

The CO₂ used was 99.99% purity (Matheson of Canada). Oxygen was prepared by decomposition of potassium permanganate. Helium was purified by passage through 13× molecular sieve at -196°C.

In most cases the preadsorption of CO₂ was conducted for 60 min, preceded by heating the catalyst *in vacuo* (10⁻⁵ torr) at 400°C for 90 min. Preliminary experiments showed that the catalyst pretreated in this manner does not desorb detectable amounts of oxygen in the temperature interval of TPD measurements.

After preadsorption of CO₂ at a given temperature the sample was treated for 15 min *in vacuo* by collecting gaseous and easily desorbable CO₂ in a liquid nitrogen trap. The helium stream was subsequently admitted to the reactor and when CO₂ desorption was no longer detectable (stable base line of the recorder connected to the catharometer), the temperature programmed desorption was conducted. The catalyst temperature was linearly increased at a rate of 18°C min⁻¹ in the temperature interval 25-450°C. From -78 to 25°C almost linear increase of the temperature was accomplished by removing the cooling mixture of solid CO₂ and ethanol from the reactor.

The TPD work was supplemented by some experiments on actual CO oxidation. These were carried out in a circulating system (850 ml volume) after pretreating 1 g of catalyst for 2 hr under vacuum (10⁻⁵-10⁻⁶ Torr) at 400°C. After this the temperature was lowered to 0°C and a stoichiometric mixture of CO + O₂ with a total pressure of 15 Torr was admitted. The CO₂ formed was frozen in a trap at

TABLE 1
TEMPERATURE DEPENDENCE OF THE ADSORBED
AMOUNT OF CO₂ OVER CO₃O₄^a

	Temp and duration of the adsorption		V ads (ml (NTP) g ⁻¹)
	°C	min	
1.	-78	30	0.115
2.	-78	60	0.115
3.	25	60	0.059
4.	25	30	0.056
5.	30	150	0.063
6.	175	60	0.051
	and cooled to 55°C		
7.	50	60	0.051
8.	103	60	0.032
9.	175	60	0.028

^a Pretreatment under vacuum at 400°C, 90 min; specific surface area of the sample 1.17 m² g⁻¹; CO₂ pressure 80 Torr.

-196°C and the reaction rate was determined by monitoring the pressure drop. These experiments established that there was a decay of activity in successive runs even when CO₂ was being frozen out. In the interval 0-100°C a very strong effect of inhibition was observed after preadsorption of carbon dioxide.

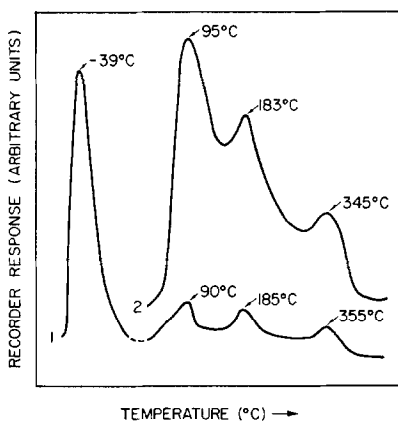


FIG. 1. TPD profiles of carbon dioxide on cobaltous-cobaltic oxide; (1) preadsorption of carbon dioxide at 24°C for 30 min and evacuation for 15 min at the same temperature before TPD; (2) preadsorption at -78°C for 60 min and evacuation before TPD 15 min at the same temperature (sensitivity of the recorder 4 times lower).

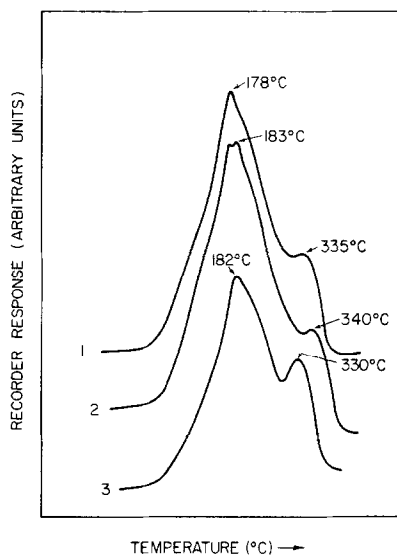


FIG. 2. TPD profiles of carbon dioxide on cobaltous-cobaltic oxide; (1) preadsorption of CO₂ at 175°C for 60 min, cooling to 50°C and evacuation before TPD 15 min; (2) preadsorption at 175°C for 60 min and evacuation before TPD for 15 min at the same temperature; (3) preadsorption at 103°C for 60 min and evacuation before TPD for 15 min at the same temperature.

The temperature dependence of the amount of CO₂ which can be adsorbed on CO₃O₄ at the experimental conditions is shown in Table 1; its magnitude increases several times by decreasing the temperature of adsorption from 170 to -78°C. The adsorption even at low temperatures is partially irreversible.

In Figs. 1 and 2 are shown the desorption spectra corresponding to the preadsorption of CO₂ at -78, 24, 103 and 175°C. Four desorption peaks were observed at -39, 90-95, 178-183, 330-350°C. The forms of CO₂ sorption corresponding to these peaks have been designated as α , β , γ , and δ , respectively.

Preadsorption at 25 and 50°C gave rise to desorption peaks at 95, 183 and 345°C (β , γ and δ forms). The last two peaks have been also observed after preadsorption at 170°C.

To establish whether the adsorption forms β and γ occupy different or identical adsorption sites, experiments were carried

out by preadsorption of CO_2 at 170°C and a slow decrease of the catalyst temperature to 30 or 50°C in presence of CO_2 . In this case the desorption peak corresponding to the β form was not observed. The disappearance of this peak is an indication that both forms occupy identical adsorption sites, in this case completely blocked by the γ form.

However, if the conditions of the preadsorption do not permit a complete blocking the β adsorption form appears again. This is illustrated by Fig. 3 recorded after admitting CO_2 at 250°C and subsequent cooling of the catalyst to -78°C . An increase of the relative amount of the form is observed. Well-pronounced, simultaneous δ and β forms are evident.

Repeated desorption measurements showed good reproducibility. Control experiments carried out by freezing out the desorbed CO_2 present in the helium stream in a trap at -196°C showed complete disappearance of all desorption peaks.

The first desorption peak can be attributed to a form of physical adsorption or a weak chemisorption, in view of its appearance at a very low temperature. In support of this view is the fact that the appearance and the area of the desorption peak is almost independent of the temperature and the duration of the preadsorption at higher temperatures.

Due to the fact that TPD has been carried out in two stages (-78 to 25°C and 25 to 450°C) the 90°C peak might be re-

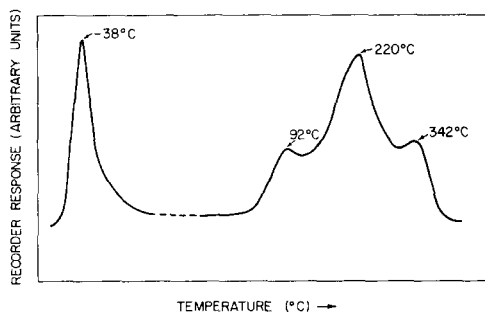
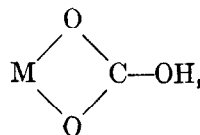


FIG. 3. TPD profile following preadsorption of carbon dioxide on cobaltous-cobaltic oxide at 250°C for 60 min, cooling the sample to -78°C and evacuation for 15 min before TPD.

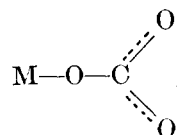
garded as a continuation of the large desorption peak at -39°C . However, it was observed also after prolonged desorption in the helium stream at a fixed temperature of 20°C . Furthermore, its area scarcely increases after an additional preadsorption of CO_2 at lower temperatures and was also observed after preadsorption of CO_2 at 25 and 50°C . All this leads to the conclusion that the form exists as a separate form of adsorption. The appearance of a desorption peak in the temperature range 90 – 110°C suggests that this adsorption form might play an important role in the low temperature CO oxidation and in the complete oxidation of organic compounds.

The last two forms of CO_2 sorption (γ and δ) show high stability. At a rate of programmed heating of the catalyst of $18^\circ\text{C min}^{-1}$ the desorption peak of the γ form has been observed near 180°C and of the δ form between 340 and 355°C .

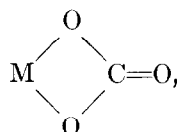
The mechanism of CO_2 sorption over Co_3O_4 in the temperature range -80 to 450°C has not been studied until now in detail. In the eminent works of the Bristol school (6, 7) on CO and CO_2 chemisorption and CO oxidation, the possible formation of a surface carbonate complex has been shown. Numerous investigations of infrared spectra of CO and CO_2 adsorbed over metal oxides (8–13) have established the formation of complexes of different types: bicarbonate



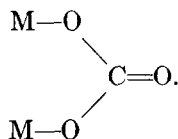
monodentate



bidentate



and bridge-like



Taking into account the high stability of the γ and δ forms, their existence can be explained by the formation of surface and even bulk carbonates.

The appearance of two high temperature sorption forms of CO_2 could be attributed to the presence on the surface and in the bulk of cations with different valency (Co^{2+} and Co^{3+}) which, respectively, provide energetically different adsorption sites.

The present study shows that the data on the catalytic activity of Co_3O_4 with respect to oxidation reactions accompanied by CO_2 formation may be influenced to a significant degree by its adsorption on the active oxide surface. The disappearance of an adsorption form from the surface could be accompanied by a change in the slope of an Arrhenius plot for the CO oxidation. It also follows, that, strictly speaking, correct kinetic data characterizing the total surface of Co_3O_4 can be obtained only at temperatures above the range of existence of the δ form. This is a condition for a constant specific activity of Co_3O_4 in the course of the oxidation of carbon-containing compounds. Less correct are data on CO oxidation obtained at temperatures only over the range of existence of γ form. At even lower temperatures the kinetic parameters strongly depend on the surface coverage of Co_3O_4 by carbon dioxide.

ACKNOWLEDGMENTS

Most of the TPD measurements were performed in the Division of Chemistry of the National Research Council of Canada, Ottawa and the author is extremely grateful to Dr. R. J. Cvetanovic and Dr. Y. Amenomiya for their

introduction to the experimental technique and for the creative and friendly atmosphere during his stay in the section of Chemical Kinetics.

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Received July 24, 1973; revised
November 29, 1973

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