

## Microcalorimetric Study of the Interaction of CO, O<sub>2</sub>, and CO + O<sub>2</sub> with Pt/SnO<sub>2</sub> and SnO<sub>2</sub> Catalysts

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The heat evolved in the interaction of CO, O<sub>2</sub>, and CO + O<sub>2</sub> with SnO<sub>2</sub> and Pt/SnO<sub>2</sub> catalysts was evaluated at different temperatures in the range 300–475 K using microcalorimetry. The effect of oxygen and hydrogen pretreatments of the samples on the heat evolved shows that in the case of Pt/SnO<sub>2</sub>, the values were higher for the oxidized sample as compared to the reduced sample, whereas the trend was reversed for metal-free SnO<sub>2</sub>. The thermochemical data reveal heterogeneity of CO or O<sub>2</sub> adsorption/reaction sites and show that the heat evolved in interaction of a gas is considerably influenced by the chemical nature of the catalyst surface and by the presence of preadsorbed species. The data support the view that the lattice oxygen abstraction from SnO<sub>2</sub> plays an important role in CO oxidation at all the catalyst temperatures under study. The presence of platinum is found to augment Sn<sup>4+</sup> → Sn<sup>2+</sup> conversion. It is suggested that the energy released in the chemisorption of carbon monoxide or oxygen over Pt gives rise to a localized temperature surge in the vicinity of metal sites and this additional source of energy leads to enhanced CO oxidation activity of Pt/SnO<sub>2</sub> via accelerated lattice oxygen abstraction. © 1990 Academic Press, Inc.

### INTRODUCTION

The catalytic oxidation of CO is known to follow different mechanistic routes depending on the catalyst system employed, as has been reviewed in several articles (1–6). It is believed that in the case of metal oxide catalysts, the CO oxidation follows a redox mechanism according to which the structural oxygen of the catalyst lattice participates directly in the reaction. The catalyst is then rejuvenated with the help of oxygen in the reactant gas stream. In the case of noble metal catalysts, the mechanism involves activation and subsequent reaction of adsorbed atomic or molecular species without direct participation of the catalyst lattice.

No unanimity of view, however, exists in the case of the CO oxidation mechanism when noble metals dispersed over oxide supports are used as catalysts. For example, in the case of Pd/SnO<sub>2</sub> catalyst interesting synergistic effects have been observed (7, 8) and the phenomenon has been attributed

to spillover of both the CO and O from palladium to SnO<sub>2</sub>. Matolin *et al.* (9), on the other hand, have provided evidence for the partial decomposition of CO over supported Pd and the formation of surface carbon as an intermediate species during the steady-state CO oxidation process. Harrison *et al.* (10) have shown the existence of metal–support interaction in Pt/CeO<sub>2</sub> catalyst and have suggested that ceria contributes to a large number of catalytic functions.

Adsorption microcalorimetry is a useful technique which is sensitive to each step responsible in a catalytic process, viz., chemisorption of reactants followed by surface transformations and desorption of reaction products. Thus, on the one hand, this technique is capable of giving information about the overall effect of various processes occurring simultaneously over a catalyst surface, and, on the other hand, the specific surface processes can be evaluated in certain cases by comparison of experiments performed under different conditions (11–13, 21). Various studies using microca-

lorimetry have been reported for CO oxidation over different oxides such as NiO and CeO<sub>2</sub> and the intermediate steps involved in CO oxidation have been proposed (14–20). Relatively fewer thermochemical studies have been carried out using supported metal catalysts (21, 22). Giamello *et al.* (21), for instance, have demonstrated that the interaction of CO and oxygen over fully reduced cupric oxide–zinc oxide catalysts involves adsorption of carbon monoxide on copper metal while redox reactions occur in a precalcined sample.

In the present study we measured the molar heat evolved ( $Q_{\text{molar}}$ ) when pulses of CO, O<sub>2</sub>, or CO + O<sub>2</sub> were admitted to Pt/SnO<sub>2</sub> and SnO<sub>2</sub> catalysts under dynamic flow of a helium carrier gas to obtain the thermochemical data under practical catalytic reaction conditions. The effect on  $Q$  values of different pretreatments given to a sample was evaluated to understand the role of different surface oxidation states on the catalytic activity. The information thus obtained has been used to delineate the reaction paths involved in CO oxidation reaction over supported metal catalysts.

#### EXPERIMENTAL

The heat evolved in the interaction of CO and CO + O<sub>2</sub> over Pt(1%)/SnO<sub>2</sub> and SnO<sub>2</sub> was measured at various isothermal temperatures in the range 300–500 K using a Calvet-type heat flow microcalorimeter (C80 calorimeter from Setaram, France) coupled with a gas chromatograph. A 100-mg sample of catalyst (around 250- $\mu\text{m}$  particle size) was taken in a recirculation stainless-steel vessel, also from Setaram, in which the sample could be evacuated or maintained under a continuous flow of H<sub>2</sub>, O<sub>2</sub>, or He carrier gas. An identical but empty calorimeter vessel connected similarly to vacuum or the gas flow system was used as a reference cell. As the sample was very small compared to the weight of the calorimetric vessel, the dissymmetry produced by using sample in only one of the cells was negligible. For introduction of an adsorbate,

injection ports were provided near the calorimeter entry points.

After the catalyst sample was subjected to the desired pretreatment, small pulse doses (100  $\mu\text{l}$  each) of adsorbate [of CO, O<sub>2</sub>, or CO + O<sub>2</sub> (1 : 1) mixture] were successively introduced at time intervals of about 15 min using a gastight hypodermic syringe while the adsorbent samples were maintained at an isothermal temperature in the range 300–500 K and under a helium carrier flow of 20 ml min<sup>-1</sup>. While the heat evolved during individual pulse injections of adsorbate over the catalyst sample was measured, effluents were analyzed using an on-line gas chromatograph. From the difference between the amounts of adsorbate injected and eluted, the amount of gas adsorbed or reacted was evaluated. It should be emphasized here that with the experimental equipment adopted, the heat evolved at a particular sample temperature corresponds to the overall effect of irreversibly held CO on the catalyst surface and also that of the CO oxidation process.

The heat change, if any, in the introduction of a gas pulse into the empty sample cell at different temperatures was found to be negligibly small and was taken into account for heat change measurements. The calorimeter response at different temperatures was calibrated using a Joule calorimeter.

Before calorimetric measurements, the catalyst samples were treated *in situ* in flowing H<sub>2</sub> or O<sub>2</sub> gas (20 ml min<sup>-1</sup>) at 475 K for 1 h and each pretreatment was followed by evacuation (475 K, 30 min) and heating of the sample for 1 h under the He carrier flow at 475 K. While the He carrier flow was maintained, the samples were cooled to the desired temperature before adsorbate pulse injections were made. The samples pretreated in oxygen and hydrogen will be designated as Pt/SnO<sub>2</sub> (ox) and Pt/SnO<sub>2</sub> (red), respectively.

He carrier gas was passed through deoxygenated catalyst and zeolite beds to remove any traces of oxygen or moisture.

The reproducibility of the data was tested

by repeating each set of experiments at least two or three times. The trend of  $Q$  value variation with temperature or that for successive adsorbate pulse injections was found to be quite reproducible. The quantitative values of heat release per gram of catalyst sample varied by about 5% but greater inaccuracy was encountered in gas chromatographic analysis of the effluent gases, particularly in experiments carried out at lower sample temperatures (i.e., <400 K). The  $Q$  values in terms of kcal mol<sup>-1</sup> may therefore be considered to be accurate within 5–10%. The positive values of  $Q$  as given in this paper indicate the heat liberated in the process. The enthalpy change values ( $\Delta H$ ) for reactions (1)–(6) in the Discussion, however, refer to the conventional norm, i.e., a negative value for an exothermic process.

#### CATALYST

The tin oxide gel was prepared by the reported method (23, 24) of precipitating hydrous tin oxide from SnCl<sub>4</sub> solutions (at 275 K) using aqueous ammonia solution. The precipitate was washed and centrifuged repeatedly and was then dried at room temperature. The material thus obtained was redispersed in water to break up large granules and was filtered and dried again at ambient temperature and then at 475 K. The 60- to 80-mesh fraction of SnO<sub>2</sub> gel had a N<sub>2</sub> adsorption BET surface area of 178 m<sup>2</sup> g<sup>-1</sup> and was used to support 1 wt% Pt. Aqueous chloroplatinic acid solution and incipient impregnation methods were employed for this purpose. The platinum was reduced to the metallic form by drying the sample and then heating in a H<sub>2</sub> flow at ~440 K. The BET area of this sample was found to be 135 m<sup>2</sup> g<sup>-1</sup>. To evaluate the effect of different pretreatments on catalyst activity for the CO oxidation reaction, a gas mixture containing approximately 10% CO, 5% O<sub>2</sub>, and the rest He was reacted over 1 g of a Pt/SnO<sub>2</sub> or a SnO<sub>2</sub> catalyst at a flow velocity of 400 ml h<sup>-1</sup> g<sup>-1</sup>. A quartz tube flow reactor of 8-mm inner diameter was used for this

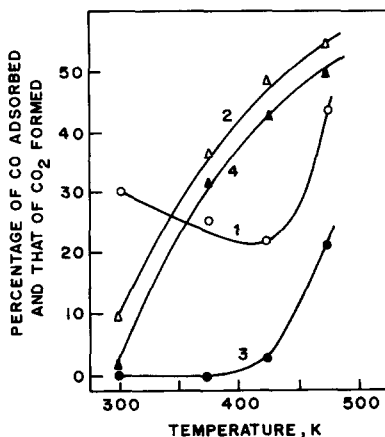


FIG. 1. Percentage of CO adsorbed/ reacted (curves 1 and 2) and percentage of CO<sub>2</sub> produced (curves 3 and 4) when a 4.9- $\mu$ mol CO pulse was injected over Pt/SnO<sub>2</sub> under helium flow. Curves 1 and 3 with Pt/SnO<sub>2</sub> (red) samples; 2 curves 4, with Pt/SnO<sub>2</sub> (ox) samples.

purpose. The effluent gases were sampled periodically and analyzed by gas chromatography.

#### RESULTS

##### *Pt(1%)/Tin Oxide Catalyst*

Interaction of carbon monoxide. The extent of carbon monoxide oxidation was found to depend on the temperature and the pretreatment given to the catalyst. When several CO pulse injections were successively made at a particular temperature, the amount of CO adsorbed/ reacted on the second pulse injection was smaller by about 10%, whereas subsequent CO injections gave identical CO adsorption data. Figure 1 shows the average amount of CO adsorbed/ reacted and that of CO<sub>2</sub> formed at different sample temperatures. A negligible amount of adsorbed CO was converted to CO<sub>2</sub> in the case of the Pt/SnO<sub>2</sub> (red) sample, particularly at temperatures below 425 K (curves 1 and 3). On the other hand, a smaller amount of CO was adsorbed over Pt/SnO<sub>2</sub> (ox) at 300 K whereas larger CO adsorption/ reaction was observed at higher sample temperatures. Adsorbed CO was almost completely

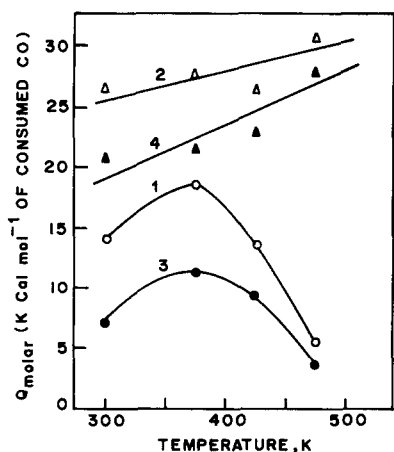


FIG. 2. Evolution of heat during exposure of a 4.9- $\mu\text{mol}$  pulse dose of CO over Pt/SnO<sub>2</sub> (red) (curve 1) and Pt/SnO<sub>2</sub> (ox) (curve 2) samples at different temperatures; curves 3 and 4 show average  $Q$  values from five successive CO pulse exposures over reduced and oxidized samples, respectively.

oxidized over Pt/SnO<sub>2</sub> (ox) at sample temperatures above 300 K (curve 4).

The heat evolved in the exposure of a CO pulse over Pt/SnO<sub>2</sub> sample depended significantly on the pretreatment condition. Curves 1 and 2 of Fig. 2 show  $Q_{\text{molar}}$  values when CO pulses were exposed over reduced and oxidized Pt/SnO<sub>2</sub> at different temperatures. It is observed that whereas in case of a Pt/SnO<sub>2</sub> (red) sample, the  $Q$  value initially increases with increase in catalyst temperature from 300 to 375 K, further increase in sample temperature reduced heat evolution drastically. With a Pt/SnO<sub>2</sub> (ox) sample, the  $Q$  values were found to be almost constant over the same temperature range.

At a particular sample temperature, when several CO pulse doses were interacted successively with an interval of about 15 min, the data given in Fig. 3 were obtained. The  $Q_{\text{molar}}$  values (per mole of CO consumed) decreased for the first two or three CO pulse injections after which almost constant values were observed.

In the case of the Pt/SnO<sub>2</sub> (ox) sample, the decrease in  $Q$  value on successive CO

pulse injections was more pronounced, as is evident from the data given in Fig. 3.

The average  $Q$  values obtained on exposure of the first five injections is shown by curves 3 and 4 in Fig. 2 for reduced and oxidized samples respectively.

*Interaction of O<sub>2</sub>.* After 8 to 10 pulse injections of CO over Pt/SnO<sub>2</sub> at a particular temperature, the sample was maintained under helium for about 30 min to remove reversibly held CO. At this stage, when oxygen pulses were admitted to the sample, a large amount of heat was evolved, particularly in the case of a sample pretreated in oxygen prior to CO exposure. The  $Q$  values were normally higher for the first O<sub>2</sub> pulse exposure, whereas a constant value was obtained from the third pulse onward. Figure 4 gives the typical temperature-dependent variation in average  $Q_{\text{molar}}$  values for the first five oxygen pulse injections as observed with the reduced and oxidized Pt/SnO<sub>2</sub> samples.

*Effect of adsorption sequence.* When the sequence of oxygen and carbon monoxide pulse injections was reversed, the  $Q$  values were significantly different. Thus, instead of introducing oxygen subsequent to CO pulse

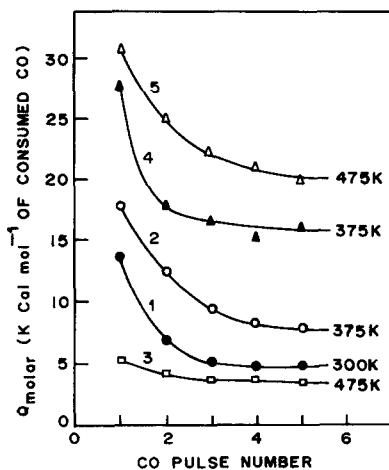


FIG. 3. Evolution of heat during exposure of successive 4.9- $\mu\text{mol}$  CO pulse doses over Pt/SnO<sub>2</sub> (red) (curves 1-3) and Pt/SnO<sub>2</sub> (ox) (curves 4 and 5) samples at different temperatures.

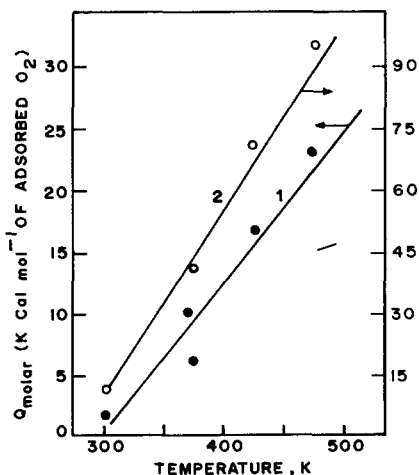


FIG. 4. Average  $Q$  values in the interaction of five successive  $4.9\text{-}\mu\text{mol}$  O<sub>2</sub> pulse injections following seven or eight injections of CO over Pt/SnO<sub>2</sub> (red) (curve 1) and Pt/SnO<sub>2</sub> (ox) (curve 2) catalysts at different temperatures.

exposures as reported above, when a Pt/SnO<sub>2</sub> (red) sample was first exposed to a series of O<sub>2</sub> pulses and then to successive pulse doses of CO, the data shown in Figs. 5a and b, respectively, were obtained. It may be noted that the  $Q$  values for oxygen pulse injections over freshly reduced sample are in the range 20 to 80 kcal mol<sup>-1</sup> for sample temperatures in the range 375–475 K (Fig. 5), whereas the corresponding  $Q$  values from a CO preexposed sample were 10

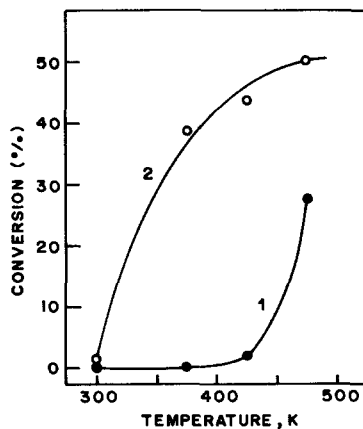


FIG. 6. Average yield of CO<sub>2</sub> when  $4.9\text{-}\mu\text{mol}$  CO + O<sub>2</sub> (1:1) pulse injections were made at different temperatures over Pt/SnO<sub>2</sub> (red) (curve 1) and Pt/SnO<sub>2</sub> (ox) (curve 2) catalysts.

to 25 kcal mol<sup>-1</sup> (Fig. 4). It is also of interest to note that the CO interaction over an oxygen covered surface gives rise to less heat evolution (Fig. 5b) as compared to that over Pt/SnO<sub>2</sub> (ox) sample.

*Interaction of CO + O<sub>2</sub> (1:1) gas mixture.* Figure 6 shows the CO<sub>2</sub> yield when a  $100\text{-}\mu\text{l}$  ( $\sim 4.9\text{-}\mu\text{mol}$ ) pulse of CO + O<sub>2</sub> gas mixture in an equimolar ratio is exposed to freshly reduced or oxidized sample at different temperatures. The data show that the CO + O<sub>2</sub> reaction is considerably influenced by the oxidation state of the catalyst sur-

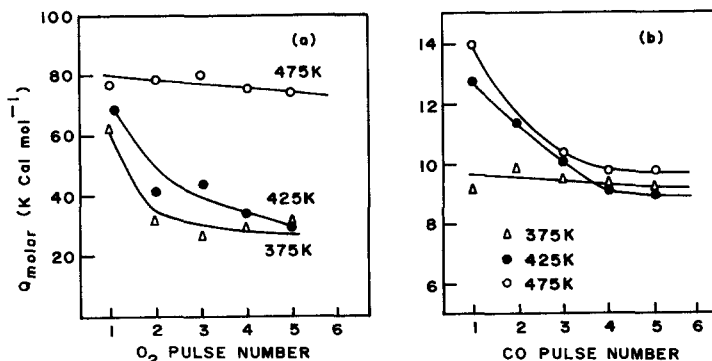


FIG. 5. Evolution of heat during exposure of successive pulse doses of O<sub>2</sub> on Pt/SnO<sub>2</sub> (red) catalyst (a) and during subsequent CO pulse exposures (b).

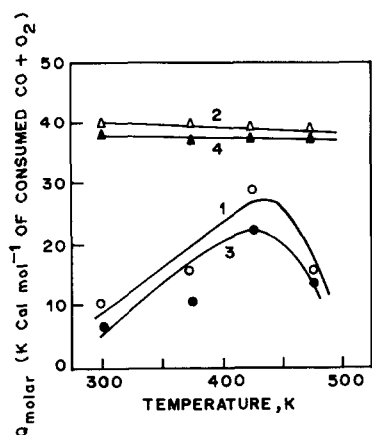


FIG. 7. Evolution of heat during exposure of a 4.9- $\mu\text{mol}$  CO + O<sub>2</sub> (1:1) gas mixture pulse over Pt/SnO<sub>2</sub> (red) (curve 1) and Pt/SnO<sub>2</sub> (ox) (curve 2) samples at different temperatures. Curves 3 and 4 show average  $Q$  values from five successive CO + O<sub>2</sub> pulse exposures.

face; much smaller amounts of CO<sub>2</sub> were formed using Pt/SnO<sub>2</sub> (red) sample as compared to those obtained with Pt/SnO<sub>2</sub> (ox) sample at all catalyst temperatures under investigation.

Figure 7 shows the amount of heat evolved in the interaction of CO + O<sub>2</sub> over Pt/SnO<sub>2</sub> (red) and Pt/SnO<sub>2</sub> (ox) samples. Although the gas mixture contains oxygen in excess of that required for stoichiometry, the  $Q$  values follow a trend almost similar to that observed in the experiments carried out with CO alone (Fig. 2). This therefore indicates that both CO and O<sub>2</sub> interact/react

independently with the catalyst surface before giving rise to CO<sub>2</sub> formation.

With the Pt/SnO<sub>2</sub> (red) sample, the  $Q$  value obtained on the first CO + O<sub>2</sub> pulse dose injection is equal to the value calculated from independent CO and O<sub>2</sub> injections, i.e.,  $Q_{\text{CO}+\text{O}_2} = Q_{\text{CO}} + Q_{\text{O}_2}$ . In the case of subsequent pulse injections, the  $Q$  values from mixture pulse injections were higher. The trend, however, reversed in the case of an oxidized sample.

#### SnO<sub>2</sub> Catalyst

Negligible amounts of CO, O<sub>2</sub>, or CO + O<sub>2</sub> were adsorbed/reacted over metal-free SnO<sub>2</sub> at temperatures below 400 K under the experimental conditions discussed above. In the higher temperature experiments, comparatively larger amounts of CO or CO + O<sub>2</sub> gas mixture reacted to form CO<sub>2</sub> with a SnO<sub>2</sub> (red) catalyst as compared to a SnO<sub>2</sub> (ox) sample. This is in contrast to the results observed for Pt/SnO<sub>2</sub> catalysts where oxidized samples were more active. Table 1 gives average yields of CO<sub>2</sub> from CO and CO + O<sub>2</sub> pulse exposures over SnO<sub>2</sub> under different experimental conditions.

Correspondingly, low  $Q$  values were observed in the interaction of CO, O<sub>2</sub> or CO + O<sub>2</sub> over SnO<sub>2</sub> at temperatures lower than 400 K. The heat evolved in the interaction of O<sub>2</sub> and CO + O<sub>2</sub> was marginally higher from reduced SnO<sub>2</sub> samples. Table 2 gives heat evolution data for the interaction of different adsorbates over SnO<sub>2</sub> at various

TABLE I

Percentage CO  $\rightarrow$  CO<sub>2</sub> Conversion When a 4.9- $\mu\text{mol}$  Pulse of CO or CO + O<sub>2</sub> Is Admitted at Different Temperatures over Reduced or Oxidized SnO<sub>2</sub> Catalyst

Temperature (K)	CO adsorbed (%)		CO <sub>2</sub> yield from CO		CO <sub>2</sub> yield from CO + O <sub>2</sub>	
	SnO <sub>2</sub> (red)	SnO <sub>2</sub> (ox)	SnO <sub>2</sub> (red)	SnO <sub>2</sub> (ox)	SnO <sub>2</sub> (red)	SnO <sub>2</sub> (ox)
303	— <sup>a</sup>	—	—	—	—	—
373	—	—	—	—	—	—
423	27.5	10.0	16.8	—	16.0	—
475	44.8	38.6	31.5	30.5	36.1	38

<sup>a</sup> —, No measurable CO adsorption or CO<sub>2</sub> formation.

TABLE 2

Heat Evolved<sup>a</sup> in the Interaction of 4.9- $\mu$ mol CO, O<sub>2</sub>, or CO + O<sub>2</sub> (1:1) Pulses over SnO<sub>2</sub> at Different Temperatures as a Function of Sample Pretreatment at 475 K in H<sub>2</sub> or O<sub>2</sub>

Temperature (K)	SnO <sub>2</sub> (red)			SnO <sub>2</sub> (ox)		
	CO	O <sub>2</sub>	CO + O <sub>2</sub>	CO	O <sub>2</sub>	CO + O <sub>2</sub>
303	2.4	0.5	6.4	0.2	0.1	0.15
373	14.0	7.6	22.0	3.5	0.3	4.0
423	(27.3)	(111.4)	(63.2)	24.0	3.0	22.0
475	35.0	24.2	58.2	(32.2)	(21.0)	(38.6)
	(31.8)	(98.5)	(49.7)			
	67.2	91.4	113.0	58.2		48.7

<sup>a</sup> Average values in kcal ( $\times 10^{-5}$ ) per gram of adsorbent. Values in parentheses represent the  $Q$  values in terms of kcal per mole of consumed gas.

sample temperatures. Since it was not possible to evaluate the amount of gas adsorbed accurately at temperatures below 400 K, the average values of heat evolved per gram of a catalyst are given in such cases for comparative evaluation. As is shown in the data of Table 2, considerably larger  $Q$  values were observed in the interaction of CO, O<sub>2</sub>, or CO + O<sub>2</sub> over SnO<sub>2</sub> at a higher temperature (475 K), particularly from a SnO<sub>2</sub> (red) sample.

The  $Q$  values expressed per mole of CO<sub>2</sub> formed in the interaction of CO and CO + O<sub>2</sub> are given in Table 3 for both Pt/SnO<sub>2</sub> and SnO<sub>2</sub> samples.

#### Catalyst Activity for CO Oxidation

*Pt/SnO<sub>2</sub>* catalyst. Curve a of Fig. 8 shows the equilibrium catalytic activity of a Pt/SnO<sub>2</sub> sample of a mixture of CO and O<sub>2</sub> (2:1) reacted continuously at a flow velocity of 400 ml h<sup>-1</sup> g<sup>-1</sup>. The sample was pretreated in He at 475 K for 1 h to remove any adsorbed moisture. On pretreatment of a sample in oxygen flow (475 K, 1 h) prior to helium treatment, the catalyst behavior remained almost unaltered (curve b, Fig. 8). However, pretreatment in H<sub>2</sub> (440 K, 1 h) following helium heating at 475 K reduced the catalyst activity considerably and no sig-

TABLE 3

Heat Evolved<sup>a</sup> in the Interaction of CO or CO + O<sub>2</sub> Pulse Injections over Prereduced Pt/SnO<sub>2</sub> and SnO<sub>2</sub> Samples at Different Temperatures

Temperature (K)	Pt/SnO <sub>2</sub> (red)		SnO <sub>2</sub> (red)	
	CO interaction	CO + O <sub>2</sub> interaction	CO interaction	CO + O <sub>2</sub> interaction
303	— <sup>b</sup>	—	—	—
373	—	—	—	—
423	18.2	58.0	44.2	140.0
475	7.5	59.2	47.3	125.0

<sup>a</sup> kcal/mol of CO<sub>2</sub> formed.

<sup>b</sup> —, unmeasurable CO<sub>2</sub> yield.

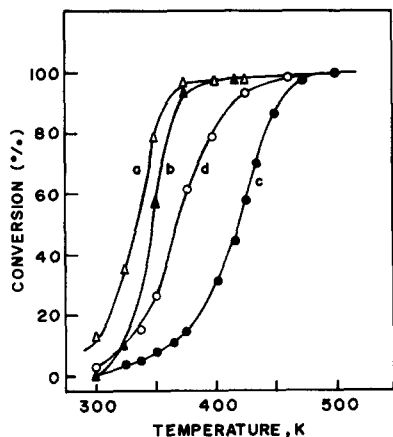


FIG. 8. Percentage yield of  $\text{CO}_2$  when 10%  $\text{CO} + 5\% \text{O}_2$  in He were reacted at different temperatures over  $\text{Pt}/\text{SnO}_2$  subsequent to pretreatment under (a) He (475 K, 1 h), (b)  $\text{O}_2$  (475 K, 1 h) followed by He (525 K, 1 h) (c)  $\text{H}_2$  (440 K, 1 h) followed by He (525 K, 1 h), (d)  $\text{H}_2$  (440 K, 1 h) followed by He (525 K, 1 h) and then further treatment under  $\text{O}_2$  (475 K, 1 h) and in He (525 K, 1 h).

nificant conversion was observed at temperatures less than 400 K, as is shown by curve c in Fig. 8. On further oxygen treatment of a reduced sample, the catalyst activity was restored though not to its original value (curve d, Fig. 8).

**Metal-free  $\text{SnO}_2$ .** An altogether different effect of pretreatment was observed in the case of a metal-free  $\text{SnO}_2$  sample. In this case, the equilibrium catalyst activity improved on pretreatment of the sample in a hydrogen atmosphere. The data in Fig. 9 represent catalyst behavior when 1 g of  $\text{SnO}_2$  sample was used for the  $\text{CO} + \text{O}_2$  reaction as a function of sample temperature.

## DISCUSSION

### *CO Adsorption and Oxidation*

**Effect of Pt metal.** The data in Table 1 show that a negligible amount of  $\text{CO}$  was adsorbed over  $\text{SnO}_2$  at temperatures below 400 K which is reflected in the poor yield of

$\text{CO}_2$  in the interaction of both the  $\text{CO}$  and the  $\text{CO} + \text{O}_2$  gas mixture pulses over  $\text{SnO}_2$  at these temperatures. It is also of interest to observe that almost all of the small quantity of adsorbed  $\text{CO}$  was converted to  $\text{CO}_2$ , indicating the participation of lattice oxygen in  $\text{CO}$  oxidation.

A comparison of the data in Fig. 1 with those in Table 1 reveals that the presence of platinum augmented  $\text{CO}$  adsorption and its oxidation over  $\text{SnO}_2$ , particularly at lower temperatures. At a higher temperature of about 475 K both  $\text{Pt}/\text{SnO}_2$  and  $\text{SnO}_2$  showed almost similar  $\text{CO}$  oxidation activity.

A similar effect of Pt metal is also reflected in  $\text{CO}_2$  yields when a  $\text{CO} + \text{O}_2$  gas mixture is admitted to  $\text{Pt}/\text{SnO}_2$  and  $\text{SnO}_2$  samples either in the form of pulse doses or in a continuous-flow mode (Figs. 6, 8, and 9). Thus, complete conversion of  $\text{CO}$  to  $\text{CO}_2$  was observed at 350 K when a stoichiometric mixture of  $\text{CO}$  and  $\text{O}_2$  was reacted over  $\text{Pt}/\text{SnO}_2$  (Fig. 8), the corresponding temperature in the case of  $\text{SnO}_2$  being about 425 K under identical sample pretreatment conditions (Fig. 9).

It thus appears that adsorption of  $\text{CO}$  on the catalyst surface is a prerequisite in the

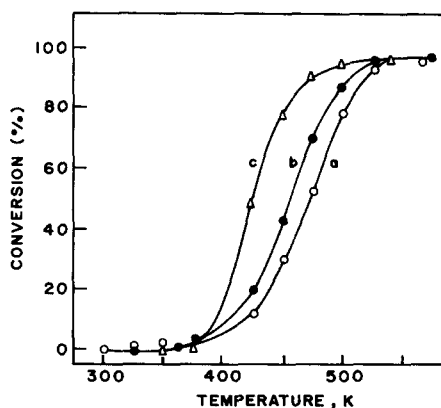


FIG. 9. Percentage yield of  $\text{CO}_2$  when 10%  $\text{CO} + 5\% \text{O}_2$  in He were reacted over  $\text{SnO}_2$  catalyst after sample pretreatments in (a) He (475 K, 1 h), (b)  $\text{O}_2$  (475 K, 1 h) followed by He (475 K, 1 h), (c)  $\text{H}_2$  (440 K, 1 h) followed by He (475 K, 1 h).



CO oxidation reaction and the presence of platinum enhances the CO chemisorption or bonding characteristics as discussed later.

*Effect of sample pretreatment.* Pretreatment of the catalyst in O<sub>2</sub> or H<sub>2</sub> had different effects on subsequent CO adsorption and oxidation properties of the Pt/SnO<sub>2</sub> and SnO<sub>2</sub> samples. In the case of the SnO<sub>2</sub> sample, hydrogen pretreatment at 475 K gave rise to enhanced CO adsorption (Table 1) and CO oxidation activity (Fig. 9). On the other hand, the amounts of CO adsorbed/ reacted over Pt/SnO<sub>2</sub> (red) samples were considerably lower than those over Pt/SnO<sub>2</sub> (ox) samples (Fig. 1), and, correspondingly, a Pt/SnO<sub>2</sub> (red) sample showed poor catalytic activity when the CO + O<sub>2</sub> gas mixture was reacted in the continuous-flow mode (Fig. 8).

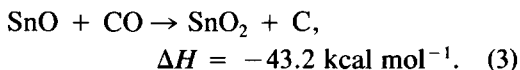
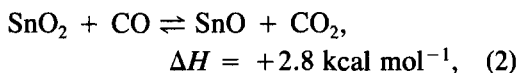
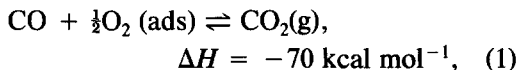
Another important aspect of the data in Fig. 1 is the almost complete conversion of CO to CO<sub>2</sub> from Pt/SnO<sub>2</sub> (ox), whereas in the case of the Pt/SnO<sub>2</sub> (red) sample only a small fraction of CO reacted to form CO<sub>2</sub>, particularly at temperatures below 400 K.

These observations clearly indicate that the oxygen chemisorbed on platinum plays an important role in the CO oxidation process.

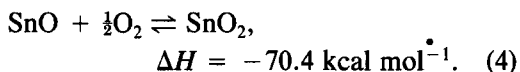
#### Heat Evolution from SnO<sub>2</sub>

The data in Table 2 show that the amount of heat evolved is considerably influenced by the pretreatment given to a sample. Thus the *Q* values in the interaction of CO and CO + O<sub>2</sub> over SnO<sub>2</sub> (red) lie in the range 25–65 kcal mol<sup>-1</sup> at sample temperatures above 400 K whereas much lower *Q* values were observed with an SnO<sub>2</sub> (ox) sample (Table 2). The higher *Q* values with the reduced sample are in agreement with the higher catalytic activity of this sample for CO + O<sub>2</sub> reaction as compared to that of an oxygen-pretreated sample (Fig. 9).

The interaction of CO with the metal-free SnO<sub>2</sub> may lead to the following processes (25):



A large heat of evolution (~90 kcal mol<sup>-1</sup>) as observed on the interaction of oxygen pulses over the SnO<sub>2</sub> (red) sample suggests the occurrence of the following reaction step as well:



None of the above processes [Eqs. (1)–(4)] can individually explain the *Q* values observed in this study (Tables 2 and 3). As it is not viable at this stage to evaluate the extent to which processes (1)–(4) or the adsorption on the sample surface may contribute to the overall reaction under particular experimental conditions, the reaction sequences giving rise to the data in Tables 2 and 3 cannot be established. Nevertheless, the temperature- and pretreatment-dependent variations in *Q* values observed in our study lead to an obvious conclusion that the interaction of CO or CO + O<sub>2</sub> is not governed exclusively by any one process but results from the simultaneous occurrence of more than one phenomenon. Similar conclusions were reached in the studies of Giamello *et al.* (21) and of Bond *et al.* (8) using different catalyst samples.

The discrepancy in *Q* values per mole of CO consumed (Table 2) and the *Q* values evaluated per mole of CO<sub>2</sub> formed in the process (Table 3) indicate that part of the reactants, products, or intermediate surface species is retained on the sample surface.

#### Heat Evolution from Pt/SnO<sub>2</sub>

*CO interaction.* The effect of platinum on the *Q* value depended on the temperature at which adsorbates were admitted to the catalyst surface. A comparison of the data

in Figs. 2 and 7 with those in Table 2 shows that much lower  $Q$  values were observed in the interaction of CO over Pt/SnO<sub>2</sub> as compared to metal-free SnO<sub>2</sub> at temperatures higher than 400 K, whereas the trend was reversed at lower temperatures. For example, in the case of Pt/SnO<sub>2</sub> (red) sample, the average  $Q$  value in the interaction of CO increases from 7 to 12 kcal mol<sup>-1</sup> while going from 300 to 375 K and decreases sharply to a value of about 4 kcal mol<sup>-1</sup> at 475 K (Fig. 2).

With a Pt/SnO<sub>2</sub> (ox) sample, an average value of about 20 kcal mol<sup>-1</sup> was observed in the interaction of CO at all the sample temperatures (Fig. 3).

*CO + O<sub>2</sub> interaction.* Similar variations in  $Q$  values were observed when a pulse of CO + O<sub>2</sub> was admitted to different samples (Fig. 7). Thus, the average  $Q$  value with the Pt/SnO<sub>2</sub> (red) sample increased from 6 to 23 kcal mol<sup>-1</sup> with a sample temperature rise from 300 to 425 K, and with further increase in temperature it reduced to a value of about 15 kcal mol<sup>-1</sup>.

In the case of the Pt/SnO<sub>2</sub> (ox) sample, the  $Q$  value was again constant at about 39 kcal mol<sup>-1</sup> for all sample temperatures.

A general conclusion may thus be drawn that the microcalorimetric data obtained in this study have a parallelism with the CO adsorption and oxidation properties of our samples.

*O<sub>2</sub> interaction.* The data in Fig. 4 show that the admission of O<sub>2</sub> pulses gives rise to vastly different heat evolution depending on the nature of the adsorbent surface. Admission of CO pulses to the Pt/SnO<sub>2</sub> (red) sample is likely to result in chemisorption of CO over Pt sites. Such a sample is expected to have a smaller capacity for oxygen chemisorption, leading thereby to low heat evolution, as is observed in the data of Fig. 4.

Another important point in Figs. 4 and 5 is the dependence of oxygen reactivity and hence of the  $Q$  value on sample temperature. This may be attributed to varying extents of O<sub>2</sub> chemisorption on Pt and of SnO → SnO<sub>2</sub> conversion at different temperatures.

*Q values from successive CO or O<sub>2</sub> pulse*

*injections.* Data in Figs. 3 and 5 show that the initial two to three CO or O<sub>2</sub> pulses gave rise to higher  $Q_{\text{molar}}$  values for both reduced and oxidized Pt/SnO<sub>2</sub> samples, whereas subsequent pulses gave rise to almost constant  $Q$  values. This observation reveals the existence of energetic heterogeneity of sites responsible for CO or O<sub>2</sub> adsorption/reaction, the more active sites being used first. A study by Harrison and Guest (24), for example, has indicated the existence of different types of hydroxyl groups over tin oxide surfaces, in agreement with our point of view.

#### *Role of Platinum*

The presence of metal on the SnO<sub>2</sub> may give rise to alternate or additional reaction routes involving chemisorption and subsequent recombination of the reactants over Pt sites following either the Langmuir-Hinshelwood or the Eley-Rideal mechanism. In such cases the  $Q$  value is expected to be greater than ~70 kcal mol<sup>-1</sup>, the actual value depending on the heat evolved in the chemisorption of CO or O<sub>2</sub> over Pt, the value of which is known to lie in the range 40–70 kcal mol<sup>-1</sup> (26). Similarly, if a part of the product CO<sub>2</sub> remained chemisorbed over the catalyst surface, the heat evolved would be equal to  $Q_{\text{CO+O}_2} + Q_{\text{CO}_2(\text{ads})}$ , i.e., more than about 100 kcal mol<sup>-1</sup>. It may thus be concluded that the reaction between chemisorbed carbon monoxide and oxygen over Pt does not govern the overall CO oxidation process in a SnO<sub>2</sub>-supported metal catalyst. The present data also indicate that the presence of platinum promotes an endothermic process which may be identified as the reaction of CO with lattice oxygen, i.e., reaction (2). Our Mössbauer spectroscopy studies (27, 28) have indeed confirmed that the presence of Pt or Pd leads to enhanced Sn<sup>4+</sup> → Sn<sup>2+</sup> conversion. It has been shown that the extent of Sn<sup>2+</sup> formation is dependent on metal content with a saturation effect at 2% Pt in SnO<sub>2</sub>. The yield of Sn<sup>2+</sup> was also found to depend on the temperature at which a sample was exposed to CO or H<sub>2</sub>. In a typical case of a Pt(1%)/SnO<sub>2</sub> sample

treated with CO or H<sub>2</sub> at 475 K, the estimated value of the Sn<sup>2+</sup> fraction, as inferred from the relative area ratio, was about 17% as compared to a value of about 10% observed for SnO<sub>2</sub> under identical conditions.

It can thus be concluded that the presence of platinum augments Sn<sup>4+</sup> → Sn<sup>2+</sup> transformation in the interaction with CO.

### Mechanism

The mechanism of the CO oxidation reaction on tin oxide-based catalysts and the nature of the transient species formed in the process have been investigated by various workers (8, 23, 24, 29, 30). An IR spectroscopy study by Thornton and Harrison (31), for example, has shown the formation of surface carbonate species in the adsorption of CO over SnO<sub>2</sub> giving rise subsequently to CO<sub>2</sub> formation on thermal desorption. No attention, however, has been paid to delineating the role of a noble-metal in augmenting CO oxidation activity of labile oxygen-containing supports such as SnO<sub>2</sub>.

Platinum may modify the CO oxidation activity of SnO<sub>2</sub> in three possible ways:

1. CO or O<sub>2</sub> molecules on activation at Pt sites spill over to adjacent SnO<sub>2</sub> sites, leading to higher reactivity.

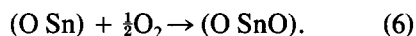
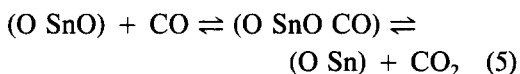
2. Energy released in the chemisorption of CO or O<sub>2</sub> molecules over Pt sites may give rise to a localized energy surge and hence temperature rise in the neighboring lattice regions where SnO<sub>2</sub>-CO reaction may occur at an accelerated rate.

3. Recombination of chemisorbed oxygen or carbon monoxide over platinum may provide an alternative route leading to the formation of surface complexes involving CO, Pt, and SnO<sub>2</sub> having different configurations.

The spillover mechanism proposed by Bond *et al.* (8) has raised more questions than it has answered, as is apparent from the published discussion on the paper. The heat values obtained in the present study also rule out the possibility of a reaction between chemisorbed CO and O being exclusively responsible for the CO oxidation

process. The studies in our laboratory have shown that the availability of additional energy in the vicinity of a metal site enhances catalytic activity of supported noble metal catalysts for the CO methanation reaction (32-34). It has been suggested that such localized energy may not necessarily give rise to a bulk temperature rise. The multiple surface temperature measurement studies by Kaul and Wolf (35, 36) have recently confirmed the existence of localized hot spots in the regions of higher CO oxidation reaction rate on Pt/SiO<sub>2</sub> and Pd/SiO<sub>2</sub>. The oscillations in CO<sub>2</sub> yields during the CO oxidation process have been attributed to fluctuating zones of high and low reaction rates. Dirk Boecker and Gonzalez (37) have similarly proposed the existence of CO islands with highly reactive boundaries in CO oxidation on Pt/SiO<sub>2</sub> and Pd/SiO<sub>2</sub>.

The data in the present study may thus be understood in the framework of the following well-known redox mechanism involving abstraction of oxygen from SnO<sub>2</sub> (23):



The parentheses represent surface species.

The effect of H<sub>2</sub> or O<sub>2</sub> pretreatment on the CO oxidation activity of metal-free SnO<sub>2</sub> catalyst (Fig. 9) and on the corresponding *Q* values (Tables 2 and 3) show that the sequence in which the above three steps [reactions (5) and (6)] occur plays an important role. Reaction (5) is an endothermic process; reaction (6) is an exothermic one. As has been discussed above, the reduced SnO<sub>2</sub> has a 2+ valence state of tin at the surface and thus the exposure of oxygen to such a sample would result in energy release to the extent of about 70 kcal mol<sup>-1</sup>. It is suggested that the energy thus released would be available to overcome requirements for the two steps in reaction (5), thus helping to sustain the overall CO oxidation reaction.

In case of Pt/SnO<sub>2</sub>, larger energies are evolved as compared to SnO<sub>2</sub> in the interaction of CO, O<sub>2</sub>, and CO + O<sub>2</sub> at sample

temperatures of 300 and 375 K. In the absence of additional data, we tentatively attribute this to the dominating role of chemisorption processes on Pt sites at these temperatures. Whether a platinum site is exposed first to O<sub>2</sub> or CO seems to play an important role in determining catalyst behavior. A comparison of the data in Figs. 4 and 5 shows that a larger amount of heat (40–80 kcal mol<sup>-1</sup>) is evolved in the interaction of O<sub>2</sub> over H<sub>2</sub> reduced Pt/SnO<sub>2</sub> as compared to a similar sample with preexposed CO (5–25 kcal mole<sup>-1</sup>). The higher catalytic activity of oxidized Pt/SnO<sub>2</sub> may thus be attributed to a reaction sequence in which chemisorption of O<sub>2</sub> over Pt rather than that of CO is favored. These observations are in agreement with several studies reported in the literature which show that CO oxidation does not occur on platinum if the surface is completely saturated with CO, whereas on a partly CO-covered surface the reaction proceeds at high rate (3).

In conclusion, we may state that the transfer of chemisorption energy from the metal particle to the support may lead to a localized temperature surge at the metal–support interface regions which may act as sites of higher CO oxidation activity. The fluctuations in the energy available around such reaction sites at a particular temperature may be responsible for the so-called self-generated oscillatory behavior of the CO oxidation reaction over platinum, as has been investigated by several authors and reviewed recently by Razon and Schmitz [6].

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#### REFERENCES

1. Katz, M., *Advan. Catal.* **5**, 177 (1953).
2. Dwyer, F. G., *Catal. Rev.* **6**, 261 (1972).
3. Boreskov, G. K., "Catalysis: Science and Technology" (J. R. Anderson and M. Boudart, Eds. Vol. 3, p. 92 (1982).
4. Golodets, G. I., "Heterogeneous Catalytic Reactions Involving Molecular Oxygen," *Studies in Surface Science and Catalysis* **15**, p. 280 (1983).
5. Morrison, S. R., "The Chemical Physics of Surfaces," p. 337. Plenum, New York, 1977.
6. Razon, L. F., and Schmitz, R. A., *Catal. Rev.-Sci. Eng.* **28**, 89, 1986.
7. Winter, E. R. S., *Advan. Catal.* **10**, 196 (1958).
8. Bond, G. C., Fuller, M. J., and Molloy, L. R., in "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 356. Chemical Society, London, 1977.
9. Matolin, V., Gillet, E., and Kruse, N., *Surf. Sci.* **186**, 541 (1987).
10. Harrison, B., Diwell, A. F., and Hallett, C., *Platinum Metals Rev.* **32**, 73 (1988).
11. Wedler, G., *J. Therm. Anal.* **14**, 15 (1978).
12. Ostrovsky, V. E., *J. Therm. Anal.* **14**, 24 (1978).
13. Della Gatta, G., *Thermochim. Acta* **96**, 349 (1985).
14. Gravelle, P. C., *Catal. Rev.-Sci. Eng.* **16**, 37 (1977).
15. Stone, F. S., *Advan. Catal.* **13**, 1 (1962).
16. Černý, S. and Ponec, V., *Catal. Rev.* **2**, 249 (1968).
17. Gravelle, P. C., *Advan. Catal.* **22**, 191 (1972).
18. Gravelle, P. C., and Teichner, S. J., *Advan. Catal.* **20**, 167 (1969).
19. El Shobaky, G., Gravelle, P. C., and Teichner, S. J., *J. Catal.* **14**, 4 (1969).
20. Breyse, M., Guenin, M., Claudel, B., and Vernon, J., *J. Catal.* **28**, 54 (1973).
21. Giamello, E., Fubini, B., and Bolis, V., *Appl. Catal.* **36**, 287 (1988).
22. Herrmann, J. M., Gravelle-Rumeau-Maillot, M., and Gravelle, P. C., *J. Catal.* **104**, 136 (1987).
23. Fuller, M. J., and Warwick, M. E., *J. Catal.* **29**, 441 (1973).
24. Harrison, P. G., and Guest, A., *J. Chem. Soc. Faraday Trans. 1* **83**, 3383 (1987).
25. Weast, R. C. (Ed.), "CRC Handbook of Chemistry and Physics," p. D77. CRC Press, Boca Raton, FL, 1979.
26. Toyoshima, I., and Somorjai, G. A., *Catal. Rev.-Sci. Eng.* **19**, 105 (1979).
27. Tripathi, A. K., Kulshreshtha, S. K., Gupta, N. M., and Iyer, R. M. in "Catalysis: Concepts and Applications—Preprints of Ninth National Symposium on Catalysis," p. 57-1. Tata McGraw-Hill, New Delhi, 1988.
28. Gangal, N. D., Kulshreshtha, S. K., Gupta, N. M., and Iyer, R. M., unpublished work.
29. Harrison, P. G., and Willett, M. J., *Nature (London)* **332**, 337 (1988).
30. Windischmann, H., and Mark, P., *J. Electrochem. Soc.* **126**, 627 (1979).
31. E. W. Thornton, and P. G. Harrison, *J. Chem. Soc. Faraday Trans. 1* **71**, 461 (1975).

32. Gupta, N. M., Kamble, V. S., and Iyer, R. M., *Radiat. Phys. Chem.* **12**, 143 (1978).
33. Gupta, N. M., Kamble, V. S., and Iyer, R. M., *J. Catal.* **66**, 101 (1980).
34. Kamble, V. S., Gupta, N. M., Natarajan, V., and Iyer, R. M., *J. Mol. Catal.* **61**, 269 (1990).
35. Kaul, D. J., and Wolf, E. E., *J. Catal.* **91**, 216 (1985).
36. Kaul, D. J., and Wolf, E. E., *J. Catal.* **93**, 321 (1985).
37. Dirk Boecker, Y. L., and Gonzalez, R. D., *J. Catal.* **110**, 319 (1988).