

Surface Interactions on Alumina-Supported Iridium Catalysts: Oxygen and Carbon Monoxide¹

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The temperature programmed desorption characteristics of oxygen, carbon monoxide, and carbon dioxide from a polycrystalline Ir ribbon and alumina-supported Ir catalysts have been studied in order to compare the catalytic oxidation of CO in the presence of oxygen adatoms and CO admolecules. On the basis of these kinetic studies a surface area titration technique for the measurement of Ir dispersions on supported catalysts is developed.

I. INTRODUCTION

To utilize the surface catalyzed oxidation of carbon monoxide for measurement of the metal surface area of supported Ir catalyst, as developed earlier for dispersed Pt catalysts (1), it is necessary to have available detailed information on the binding states of the adsorbed species, their surface populations, and their surface reactivities.

Previous sorption studies (2) with oxygen on a polycrystalline Ir ribbon had demonstrated two binding states for oxygen. The maximum surface coverage with oxygen adatoms corresponds to a ratio of O/Ir(s) = 0.61 [where Ir(s) refers to a surface iridium atom], assuming an Ir surface with an equal distribution of low-index planes of (111), (110), and (100) orientation. Brooks (3), in his room temperature adsorption measurements on an Al₂O₃-supported Ir catalyst (28.0 wt% Ir), found at saturation coverage for the ratio of the number of

atoms of atomic hydrogen adsorbed to that of oxygen H/O = 1.48, and for H/CO = 1.92. When one assumes that the hydrogen atoms occupy a monolayer corresponding to H/Ir(s) = 1.0, one calculates from these data O/Ir(s) = 0.67 and CO/Ir(s) = 0.52. The latter value compares with CO/Ir(s) \cong 0.5 deduced from infrared data for a silica-supported Ir catalyst (4). It becomes apparent from these data that the bonding of CO admolecules and O adatoms represents a distribution of surface configurations involving adsorption to single and multiple Ir atoms. As a result, the maximum surface coverage with each of these adspecies per Ir atom is less than unity.

To gain further insight into the kinetics of the surface catalyzed oxidation of CO, and its potential as a technique for surface area determination by "titration," a series of sorption and reaction studies was carried out with polycrystalline Ir ribbons and Al₂O₃-supported Ir catalysts³ containing various weight loadings of Ir metal. The experiments included (a) temperature pro-

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grammed desorption (TPD) studies of the adspecies resulting from exposure of Ir/Al₂O₃ and Ir to CO, O₂, and CO₂, and (b) carbon monoxide oxidation kinetics by reaction involving presorbed oxygen ("forward titration" O(s) + CO → CO₂) and presorbed CO ("reverse titration," CO(s) + ½O₂ → CO₂).

II. EXPERIMENTAL DETAILS

A. Ultrahigh Vacuum Equipment

TPD from a polycrystalline iridium foil was studied in an ultrahigh vacuum system previously described (5). The Vacion-pumped system contained quadrupole mass spectrometer, ionization gages, and variable leak valves to admit gases to the system. A polycrystalline ribbon (0.0046 × 0.070 × 6.9 cm) of iridium (99.9% purity) was suspended in a catenary loop from glass-shielded tungsten leadthroughs to the reactor which connected to the mass spectrometer by way of a calibrated leak. The ribbon was heated by passage of an electric current. The leadthroughs and connectors were relatively massive and experienced little temperature rise. The temperature of the ribbon was measured with a Chromel-Alumel thermocouple (0.003 in. wire diameter) spotwelded to its center.⁴

Under dynamic flow conditions carbon monoxide, oxygen, and carbon dioxide were allowed to adsorb at chamber pressures ranging from 10⁻⁸ to 10⁻⁷ Torr. Subsequently, for desorption studies the system was pumped down to its background pressure (~10⁻⁹ Torr) before the ribbon was heated at a linear rate. The desorption rate was monitored with the mass spectrometer previously calibrated by exposure to each of the gases under study. During this period the reactor walls remained at room temperature and no wall desorption was detectable.

⁴ Conductive heat losses by this thermocouple were insignificant.

B. Temperature Programmed Desorption from Ir/Al₂O₃

Since the details of the apparatus have been presented elsewhere (6) only a brief description is given here. A 0.1 to 0.2 g sample of Ir/Al₂O₃ catalyst was placed onto the fritted disc of a cylindrical Vycor microreactor. Helium, after passage through a molecular sieve trap, cooled by liquid nitrogen, flowed over the catalyst at atmospheric pressure. The catalyst was heated by a Nichrome heater in close contact with the outer walls of the reactor. The temperature was measured by a Chromel-Alumel thermocouple in contact with the catalyst particles. The catalyst temperature was programmed to increase at prescribed linear rates. On the downstream side of the reactor, samples of the gas mixture entered the mass spectrometer through a calibrated leak located in close proximity to the reactor.

For adsorption studies known volumes of carbon monoxide or carbon dioxide were introduced into the helium stream with gastight syringes and allowed to flow over the catalyst. Injections of 1000 μl aliquots of a given gas were continued until saturation coverage was attained as manifested by a reproducible constant signal on the mass spectrometer of a magnitude corresponding to an initial aliquot in the absence of catalyst.

The same system was used in the study of CO oxidation. Oxygen (or CO) was adsorbed on the surface at room temperature, and the CO₂ formed after exposure to CO (or O₂) at room temperature or elevated temperatures was observed with the mass spectrometer.

C. Pulse Microreactor Studies

In addition, adsorption and surface reaction experiments were performed in a pulse microreactor system at a pressure of 50 psi. The Ir/Al₂O₃ catalyst samples were ground to a powder and supported on the

Pyrex frit of a tubular glass microreactor. The reactor was surrounded by a furnace and was connected to a switching valve, which allowed the catalyst to be pretreated, and then placed in the gas chromatograph helium carrier stream. A pulse valve located upstream allowed the injection of constant volume pulses of gas (O_2 or CO), which, after passage over the catalyst bed, entered the gas chromatograph for product analysis.

D. Materials

To determine the concentration of surface impurities on the iridium ribbon we employed an Auger electron spectrometer. The major surface impurities detected by this means were carbon and oxygen. In our system the Auger signal due to carbon was reduced to the noise level by heating to 1300 K in a stream of O_2 at 10^{-7} Torr for 10 min (7, 8). However, a small residual oxygen signal remained even after extensive annealing in vacuum and flashing in CO to 1300 K. It was estimated that this oxygen corresponded to less than 0.1 monolayer.

The Ir/ Al_2O_3 catalysts contained 10 and 32 wt% iridium. Surface analysis by Auger electron spectroscopy showed Ir, O, and Al

peaks. Also, a small carbon impurity peak was detected.

The O_2 was of ultrahigh purity (99.9% minimum, Linde), the CO was ultrapure (99.18% minimum, Matheson), and the CO_2 was "bone dry" (99.8% minimum, Linde). The O_2 and CO_2 were used from the cylinders without further purification. The CO was passed through a trap loaded with glass beads and cooled in dry ice-acetone for removal of metal carbonyls.

III. EXPERIMENTAL RESULTS

A. Desorption from Polycrystalline Iridium

Oxygen, carbon monoxide, and carbon dioxide were each separately adsorbed on the polycrystalline ribbon previously reduced in H_2 at 625 K and cooled to room temperature in He. The TPD data were collected as the ribbon was rapidly heated at 400 K s^{-1} from 300 to 1475 K. Carbon monoxide adsorbed readily on the iridium ribbon and it desorbed with a peak temperature of 650 K. Saturation coverage was found to be 7.1×10^{14} molecules/cm², corresponding to $CO/Ir(s) = 0.5$ assuming an equal distribution of low-index planes (100), (110), and (111), equivalent (9) to a site density of 1.4×10^{15} Ir atoms/cm².

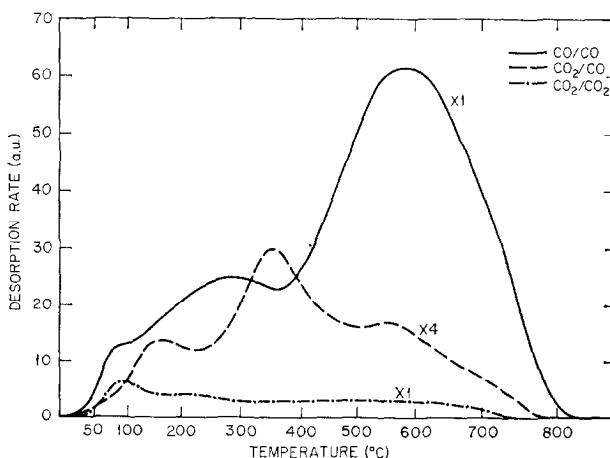


Fig. 1. TPD curves after CO saturation coverage of Ir/ Al_2O_3 catalyst at 300 K (Ir wt loading = 32 wt%; heating rate = 1.65 K s^{-1}).

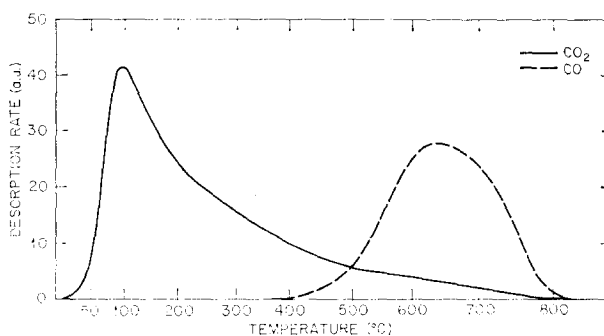


Fig. 2. TPD curves for adspecies after surface reaction; $\text{CO}(\text{g}) + \text{O}(\text{s}) \rightarrow \text{CO}_2$ (forward titration) at 300 K (heating rate = 1.65 K s^{-1}).

Carbon dioxide hardly adsorbed on iridium, and its saturation coverage was found to be very low. Exposure to O_2 resulted in rapid adsorption at 500 K with a sticking probability of ~ 0.03 , somewhat lower than the value of 0.13 reported in Ref. (2). At high oxygen coverage the peak desorption rate was found to occur at 1200 K. From the integrated area under the desorption rate versus temperature curve an oxygen coverage of 2.5×10^{14} oxygen atoms/cm² was calculated. Such a low oxygen coverage may have been caused by the formation of strongly bound surface oxygen as suggested by the results of Ageev and Ionov (3). To establish the existence of such an oxygen adlayer following O_2 desorption and TPD in vacuum to 1500 K, we exposed the iridium ribbon to CO after cooling to room temperature. Subsequent TPD gave rise to a CO_2 peak at 450 K, and repeated exposure to CO at room temperature followed by TPD generated additional CO_2 , which in the aggregate amounted to $\text{O}/\text{Ir}(\text{s}) > 0.4$.

B. Desorption from Ir/Al₂O₃ Catalyst

The Ir/Al₂O₃ catalyst was reduced in H_2 for 2 hr at 625 K and heated in He at the same temperature for 30 min preceding exposure to pulses (1000 μl) of CO until attainment of saturation coverage corresponding to $(340 \pm 40) \times 10^{-6}$ mole CO/g

catalyst. The TPD experiments at a heating rate of 1.7 K s^{-1} yielded 280 $\mu\text{moles CO/g}$ and 50 $\mu\text{moles CO}_2/\text{g}$ catalyst; i.e., a small amount of the adsorbed CO disproportionated during the heating cycle. When account is taken of the disproportionation reaction $2\text{CO} \rightarrow \text{C}(\text{s}) + \text{CO}_2$, one finds for the total mass of CO desorbed a value of 380×10^{-6} mole CO/g catalyst comparable to the amount initially adsorbed.

The TPD results⁵ for CO/CO (Fig. 1) demonstrated several binding states for CO, with a major desorption peak at 875 K (Fig. 1). For CO_2/CO a less strongly bound state with a desorption peak temperature of 625 K was observed.

On exposure of the reduced catalyst sample to gaseous CO_2 little adsorption was detectable (less than 30×10^{-6} mole CO_2/g catalyst). Also, this adsorbate was very weakly bound, as demonstrated by a peak desorption temperature of only 350 K.

C. Surface Reaction between Carbon Monoxide and Oxygen

A series of "forward titration" experiments was carried out on the Ir/Al₂O₃ catalyst using the TPD apparatus and the pulsed microreactor. After reduction of the

⁵ A shorthand notation for flash desorption spectra presented earlier is employed. For example, the notation A(α)/B refers to the α state of desorbing gas A during a programmed heating following the adsorption of gas B.

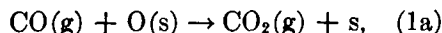
TABLE 1
Kinetics of CO Oxidation on Ir/Al₂O₃^a

Surface reaction	Temp. (K)	Product formed CO ₂ (moles/g cat) × 10 ⁴	Adspecies remaining ^b (TPD)	
			CO	O
O(s) + CO(g) → CO ₂ (g)	300	233	+	+
	373	323	+	+
	423	397	+	-
CO(s) + ½O ₂ (g) → CO ₂ (g)	300	330	+	+
	373	401	-	+
	423	399	-	+

^a Metal weight loading: 32% Ir, catalyst (Shell-405) prepared by Shell Development Co.

^b (+) Presence of adspecies, (-) its absence.

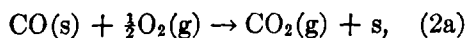
catalyst in H₂ and flushing in He, oxygen was admitted until saturation coverage was reached at 300 K. Then the catalyst was exposed to a number of separate CO pulses (1000 μl, 10 vol% CO in He), and the amount of carbon dioxide formed at room temperature was measured. Pulsing with CO was continued until no additional CO₂ was detected. In a series of runs, both the CO₂ formed and the CO consumed in the reaction were determined. The surface reaction proceeded in accordance with reaction (1).



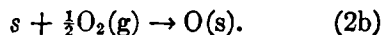
where (s) represents a surface site and (g) a gas-phase molecule. Reaction (1) is followed by the formation of a CO adlayer on the sites vacated by the oxygen adatoms:



Also, a series of measurements was carried out using the "reverse titration." First, carbon monoxide was adsorbed on the surface to saturation coverage and the catalyst surface was then exposed to O₂ at room temperature. In this case carbon dioxide is formed according to the stoichiometry:



followed by additional O₂ consumption due to:



Although reactions (1a) and (2a) occur at room temperature; (1a) proceeds at a significantly faster rate than (2a), as had previously been noted (2).

To determine the surface population of adspecies following the titration reaction a series of TPD experiments was performed after the "forward titration" at room temperature (Fig. 2). Now the CO desorption curve exhibits only the high-temperature peak (875 K) (Fig. 1), and the CO coverage is significantly reduced from that observed previously after exposure of the clean catalyst sample to CO (Fig. 1, CO/CO). However, following the titration a CO₂ desorption peak is observed (Fig. 3) which is larger and at a different temperature than the CO₂/CO₂ peak (Fig. 1). Similar results are obtained in a TPD study following the "reverse titration" at room temperature.

These TPD results point to the existence of a residual mass of adsorbed oxygen and CO following titration at 300 K. As the temperature is increased, the remaining oxygen adatoms interact with the CO admolecule by way of a Langmuir-Hinshelwood mechanism. As shown by the data in Table 1, a temperature of 423 K appears to be most suitable for this interaction between surface adsorbed species under our experimental conditions.

IV. DISCUSSION

The information derived from the TPD results is most valuable in developing a titration procedure for measurement of the Ir metal dispersion of supported catalysts. For this purpose the utility of a surface reaction specific to the metal depends on two basic requirements: (a) complete and rapid reaction between the adspecies on the metal surface on exposure to the titrating gas and complete desorption of the product in accordance with a known surface stoichiometry, and (b) knowledge of the saturation surface coverage of the adspecies before titration. Temperature programmed desorption following titration offers an excellent way of ascertaining whether these criteria are satisfied.

As indicated in Fig. 2, following oxygen adsorption and room temperature exposure to carbon monoxide (i.e., exposure to CO until no additional CO₂ formed), only a fraction of the oxygen adatoms (about 50%) reacted to form CO₂. However, upon heating, the residual O(s) is able to interact with chemisorbed CO by way of a Langmuir-Hinshelwood mechanism. Under these conditions the CO₂ peak temperature location is somewhat higher than that observed for CO₂/CO₂ (Fig. 1). Also, the total mass of CO₂ formed is considerably greater than the saturation surface coverage for CO₂/CO₂.

It is concluded that the large CO₂ peak seen in TPD after the forward titration is due to the surface reaction involving O(s) and CO(s). At temperatures in excess of 400 K the diffusional surface mobilities of the adspecies (CO and O) appear to be sufficiently great to permit reaction by a Langmuir-Hinshelwood process.

These results were applied to the measurements of metal surface area of Ir/Al₂O₃. Both forward and reverse titrations were carried out over a temperature range from 300 to 423 K. For those titrations performed at 300 K, the sample was subsequently heated at 423 K to complete the surface

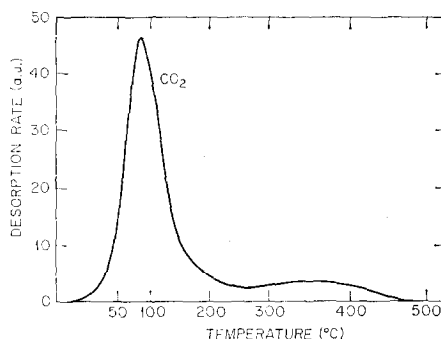


Fig. 3. TPD curve for CO₂ after surface reaction; $\frac{1}{2}\text{O}_2(\text{g}) + \text{CO}(\text{s}) \rightarrow \text{CO}_2$ (reverse titration) at 300 K (heating rate = 0.75 K s⁻¹).

reaction of the adspecies (Table 2). As predicted by the TPD data, the forward titration with gaseous CO at 300 K is inadequate to remove all the oxygen chemisorbed on the metal surface. Approximately one half of the oxygen adatoms are retained by the surface under these conditions. On raising the surface temperature to 423 K, we find that further reaction takes place between the residual adsorbed oxygen and some of the CO adsorbed during the forward titration at 300 K. The total mass of CO₂ formed amounts to an average of $(180 \pm 10) \times 10^{-6}$ mole CO₂/g catalyst.

As for the reverse titration, the problem of complete reaction of the adsorbed CO by reaction with oxygen does not exist as long as the temperature is >373 K (Table 2). However, the mass of CO₂ formed under these conditions is found to be $(140 \pm 2) \times 10^{-6}$ mole/g of catalyst, some 20% less than found in the forward titration. Undoubtedly, this difference arises from variations in saturation surface coverage with the initial adsorbate, O(s) in the forward and CO(s) in the reverse titration. As noted earlier, at saturation coverage for the Ir/Al₂O₃ one finds a ratio O/Ir = 0.67 at 300 K (8). This value may be interpreted to represent a distribution of oxygen adatoms bound to single surface Ir atoms and possibly to two nearest or next-nearest neighbors of Ir atoms (depend-

TABLE 2
Surface Area Measurement by CO/O₂ Titration of Ir/Al₂O₃^a

Expt.	Temp. (K)	Catalyst mass (g)	Initial adsorbate		Reactant		CO ₂ (moles/g cat) × 10 ⁶			Surface area (m ² /g Ir)		
			CO	O ₂	CO	O ₂	300 K	423 K	Total	m ² /g cat		
										300 K	423 K	Total
1	300	0.0210	—	X	—	86	—	—	11.1	—	11.1	111
2	300	0.0210	—	X	—	90	83	173	11.6	10.7	11.2 ^c	112
3	300	0.0210	—	X	—	89	102	191	11.5	13.2	12.3 ^c	123
4	373	0.0210	X	—	X	—	140 ^b	140	—	12.1	12.1	121
5	423	0.0210	X	—	X	—	139	139	—	12.0	12.0	120
6	423	0.0166	X	—	X	—	141	141	—	12.1	12.1	121

^a 10 wt% Ir; catalyst prepared by Shell Development Co.

^b At 373 K.

^c Average of values at 300 K and 423 K.

TABLE 3
Surface Area of Ir/Al₂O₃ Catalysts^a

Ir/Al ₂ O ₃ catalyst (Ir wt%)	History	Surface area (m ² /g Ir)
10	Fresh	120
32	Fresh	154
	Used ^b	130
	Used ^c	83
32	Fresh	185

^a Catalysts (Shell-405) prepared by Shell Development Co.

^b After exposure to 1 mole N₂H₄.

^c After intermittent exposure to 1000 moles N₂H₄.

ing on crystal orientation). Loosely, we may refer to these binding geometries as linear (λ)- and bridge (β)-bonded configurations. For O/Ir = 0.67 one calculates a distribution of two O(λ) adatoms requiring two Ir sites, and two O(β) adatoms requiring four Ir sites, or a total of six Ir atoms. With reference to the forward titration we may now conclude that one of these surface configurations, most likely the more weakly bound O(λ) adatoms, reacts readily with CO at room temperature, thereby vacating two of the Ir adsorption sites. The O(β) adatoms require a higher temperature for their reaction with neighboring CO admolecules. Since oxygen adsorption at 300 K involves an equal number of O(λ) and O(β) adatoms, the amount of CO₂ produced from each of these configurations is equal, as borne out by the experimental results on comparing CO₂ formed at 300 and 423 K (Table 2). Thus to calculate the number of Ir surface sites from the CO₂ produced in the forward titration one needs to multiply the number of CO₂ molecules generated at 300 K by a factor of 3. On the other hand, when account is taken of the total CO₂ formed at 300 and 423 K, the Ir surface site density is equal to 1.5 times the total CO₂ molecules formed. For the reverse titration the CO/Ir(s) = 0.5, i.e., a predominance of CO(β) admolecules bonded via the C atom

(and possibly also the O atom in a lying-down configuration) to two neighbor Ir atoms on the surface. As a result, the Ir surface area is given by twice the number of CO₂ molecules produced. Consideration of these configurational aspects of the adsorbate species leads to good agreement between the surface areas calculated for the forward and reverse titrations (Table 2). In Table 3 we have listed the Ir metal surface areas measured for a number of Ir/Al₂O₃ catalysts with different weight loadings of Ir.

In conclusion, the surface reaction involving the oxidation of CO offers a suitable means of surface area measurement of metallic Ir dispersion on an alumina support. Preferably by reacting chemisorbed CO with gas-phase oxygen at 423 K, rather than chemisorbed oxygen with CO, a rapid surface reaction takes place, which yields a quantitative measure of metal dispersion. The number of CO₂ molecules produced in the reaction is directly related

to the surface density of Ir atoms when account is taken of the geometrical configuration of the CO admolecules at saturation coverage preceding the titration.

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