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Supported Metal Catalysts: Preparation, Characterisation, and Function

II. Carbon Monoxide and Dioxygen Adsorption on Platinum Catalysts

S. JACKSON,*[,1] B. M. GLANVILLE,* J. WILLIS,* G. D. MCLELLAN,† G. WEBB,†[,1]
R. B. MOYES,‡ S. SIMPSON,‡ P. B. WELLS,‡[,1] AND R. WHYMAN§[,1]

*ICI Katalco, Research and Technology Group, P.O. Box 1, Billingham, Cleveland TS23 1LB, United Kingdom; †Department of Chemistry, The University, Glasgow, G12 8QQ, Scotland; ‡School of Chemistry, The University, Hull HU6 7RX, United Kingdom; and §ICI Chemicals and Polymers, Ltd., Research and Technology Department, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE, United Kindgom

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The adsorption of carbon monoxide, dioxygen, and dihydrogen on three platinum catalysts (0.89% w/w Pt/alumina, 0.75% w/w Pt/silica, and 0.48% w/w Pt/molybdena) prepared by impregnation and one catalyst (0.52% w/w Pt/molybdena) prepared by co-crystallization has been studied. On Pt/alumina and Pt/silica, three states of adsorbed carbon monoxide have been detected, one weakly held at 293 K and two strongly held. Of the two strongly adsorbed species, one is linearly bonded, the other bridge bonded. Over 80% of the strongly held material is able to exchange with gas-phase carbon monoxide. On the Pt/alumina, adsorption of submonolayer quantities of carbon monoxide results in a modification of the binding energy of surface hydrogen such that the hydrogen can be displaced by subsequent adsorption of carbon monoxide. Carbon monoxide reacts with hydroxyl groups of the support during thermal desorption from Pt/alumina to form carbon dioxide and dihydrogen. An activation energy barrier was observed for carbon monoxide adsorption on Pt/silica within the temperature range 256–297 K. Pt/molybdena prepared by co-crystallization adsorbed carbon monoxide but not dioxygen.

INTRODUCTION

The preparation and physical characterisation of a number of platinum catalysts was described in Part I (*1*). This paper reports part of the chemical characterisation of four samples, namely, Pt/alumina, Pt/silica, and Pt/molybdena, prepared by impregnation, and Pt/molybdena prepared by co-crystallization. Carbon monoxide adsorption has been studied by static and pulse-flow techniques, incorporating both stable and radioactive isotopes, and the infrared spectra of adsorbed carbon monoxide have been recorded. The adsorption of dioxygen, and its interaction with carbon monoxide and with dihydrogen, has also been examined.

EXPERIMENTAL

Nomenclature

A standard nomenclature has been adopted to designate the catalyst preparation method. Catalysts designated (I) have been prepared by impregnation, catalysts designated (C) have been prepared by co-crystallization. The units used throughout this series of publications are molecules g^{-1}, where the weight refers to the total weight of the catalyst as distinct from the weight of metal. All ratios of platinum to adsorbed gas, e.g., Pt:CO, refer to total number of platinum atoms, a subscript "s" being used to denote when only surface platinum atoms are being considered.

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[1] To whom correspondence should be addressed.

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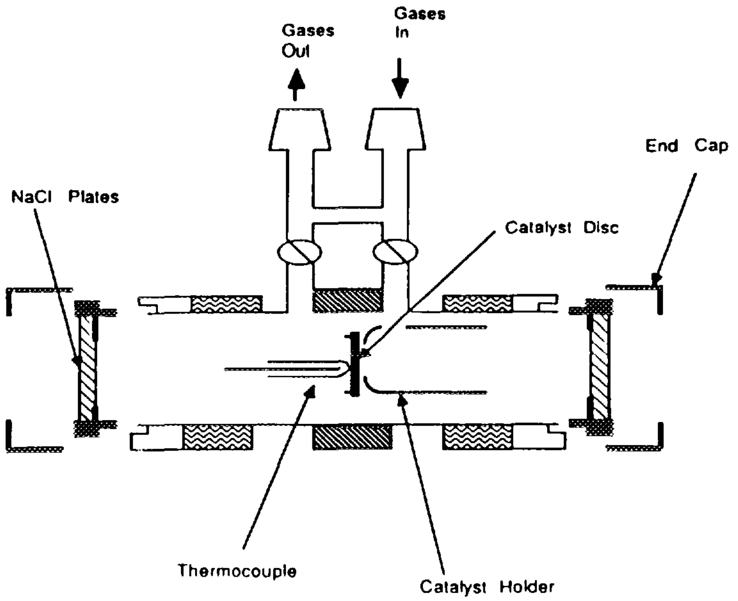

FIG. 1. *In situ* FTIR flow cell.

Apparatus and Procedures

Chemisorption studies were performed in a dynamic mode using a pulse-flow microreactor system. Using this system the catalysts (typically 0.3–0.5 g) could be reduced *in situ* in flowing 5% dihydrogen in dinitrogen by heating to 573 K at 7 K min^{-1}. When reduction had ceased the flow was changed to helium (60 cm^3 min^{-1}) and the catalyst was held at 573 K until no dihydrogen could be detected in the effluent. The catalyst was cooled, maintained in flowing helium and the adsorptive was admitted by injecting pulses of known size (typically 2 cm^3, 6.67 × 10^3 Pa, or 0.05 cm^3, 0.101 MPa) into the helium carrier-gas stream and hence to the catalyst. The amount of gas adsorbed, from any pulse, was determined from the difference between a calibration peak area and the peak area obtained following the injection of pulses of comparable size onto the catalyst. Typical detection limit for adsorption was 2×10^{16} molecules g^{-1}. Desorptions were performed by heating the catalyst to 573 K in flowing helium. After thermal desorption the catalyst was cooled in flowing helium. Adsorptions and desorptions were followed using a gas chromatograph fitted with a thermal conductivity detector and Porapak Q column coupled to a mass spectrometer (Spectramass SM100D, having a high-resolution RF head).

Chemisorptions, using ^{14}C-carbon monoxide in a static system, were determined at ambient temperature and at pressures up to 133 Pa. The system used was of similar design to that described elsewhere (*2*).

Infra-red spectra were obtained in either transmission or diffuse reflectance modes using a Nicolet 5DXC FTIR spectrometer. The instrument was set up for 2 cm^{-1} resolution using a TGS detector for transmission measurements and a liquid-dinitrogen-cooled MCT detector for diffuse reflectance measurements. A Barnes DRIFTS cell, fitted with an environmental chamber, was used for the diffuse reflectance measurements. For the transmission studies an *in situ* heatable flow cell (Fig. 1), of similar design to that described by Moon *et al.* (*3*), was developed.

Pt/alumina and Pt/silica catalysts were

examined by infrared spectroscopy in the transmission mode and were reduced *in situ* in a flow of 6% dihydrogen in dinitrogen at 573 K for 2 h. The Pt/molybdena catalysts were not susceptible to infrared examination by transmission and were studied by diffuse reflectance. Samples were mixed with diamond powder (typically 1 : 5 dilution) to improve the reflectance and then reduced statically in 3.47 × 10^4 Pa dihydrogen at 573 K for 2 h.

RESULTS

Carbon Monoxide Adsorption

Platinum/alumina (I). The adsorption of carbon monoxide on Pt/alumina was measured by pulsing aliquots of gas over the sample as described above at 294 and 273 K (see Table 1). The amount of carbon monoxide adsorbed, at both temperatures, was $(1.979 \pm 0.108) \times 10^{19}$ molecules g^{-1}, giving a $CO_{(ads.)}$: Pt ratio of 0.72 : 1.

On a pulse-by-pulse analysis of carbon monoxide chemisorption it was observed that the second and third pulses of carbon monoxide displaced dihydrogen from the catalyst. However, no species was displaced/desorbed when the first pulse of carbon monoxide adsorbed on the catalyst. When adsorption had ceased the catalyst was heated to 573 K in flowing helium, with the effluent being passed through a trap at 77 K. Dihydrogen and carbon monoxide were detected in the reactor effluent and the carbon monoxide desorption profile is shown in Fig. 2. On warming the trap carbon dioxide was detected (4.60×10^{18} molecules CO_2 was desorbed; $CO_{(ads.)} : CO_{2(des.)}$ = 4.3 : 1). The catalyst was then cooled and the carbon monoxide chemisorption repeated.

As in the initial adsorption sequence, no dihydrogen was displaced by the first pulse but dihydrogen was displaced by the second pulse of carbon monoxide. Once adsorption ceased (CO adsorbed, 1.036×10^{19} molecules g^{-1}) the catalyst was again heated to 573 K in flowing helium but the effluent was not passed through a trap. The desorption profiles are shown in Fig. 2, and it can be seen that there is coincident desorption of carbon dioxide and dihydrogen; the $CO_{(ads.)} : CO_{2(des.)}$ ratio was 2.3 : 1. This adsorption–desorption cycle was repeated with identical results. On the fourth adsorption cycle, however, no dihydrogen was displaced by the carbon monoxide; the thermal desorption was identical to the previous ones.

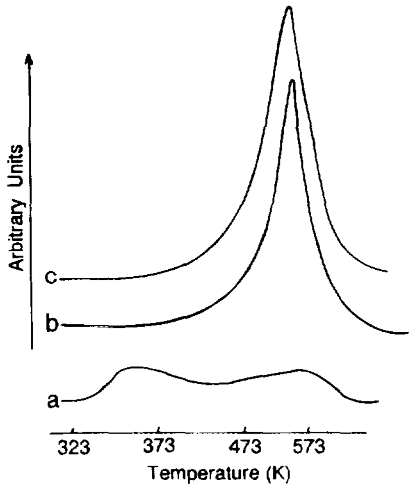

FIG. 2. Desorption profiles, after CO adsorption on Pt/alumina, of (a) CO by GC analysis, after effluent gas had been passed through a trap at 77 K; (b) H_2 by MS analysis; and (c) CO_2 by MS analysis when desorption was performed without a trap.

The ^{14}C-carbon monoxide chemisorption isotherm for Pt/alumina is presented in Fig. 3 (curve a). This was obtained at 298 K for catalyst reduced in flowing dihydrogen at 573 K. Evacuation of the saturated sample for 0.5 h resulted in a loss of 26.6% of the adsorbed carbon monoxide. Subsequent admission of 6.67 kPa of ^{12}C-carbon monoxide to the evacuated system resulted in removal of 84% of the remaining surface radioactivity.

The spectrum of carbon monoxide adsorbed on Pt/alumina was found to consist of two bands with maxima at 2076 and 1857 cm^{-1} (Fig. 4). Spectra recorded at higher temperatures revealed that adsorbed carbon monoxide could still be detected up to

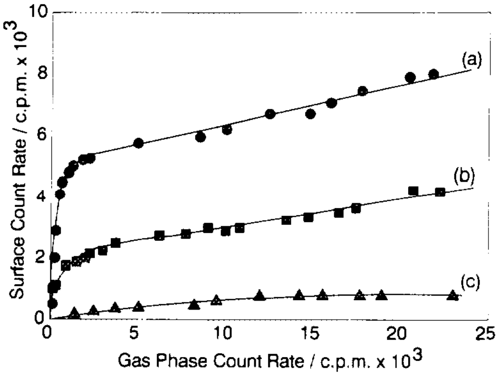

FIG. 3. ^{14}C-carbon monoxide adsorption isotherms obtained with Pt/alumina (I) (0.6281 g: curve (a)), Pt/silica (0.628 g; curve (b)) and Pt/molybdena (I) (0.628 g; curve (c)) at 293 K (^{14}CO specific activity = 0.203 mCi mmol^{-1}).

523 K. The infrared spectrum of carbon monoxide adsorbed on reduced Pt/alumina at 298 K was obtained only after considerable experimental effort. A separate paper will address the interpretation of the complex spectra obtained.

Platinum/silica (I). The adsorption of carbon monoxide on Pt/silica was measured at 294, 273, and 256 K (see Table 1). As temperature was decreased the amount of carbon monoxide adsorbed decreased, indicative of an activated adsorption. The activation energy was calculated to be 21 ± 3 kJ mol^{-1}.

A pulse-by-pulse analysis of carbon monoxide chemisorption at 294 K revealed that, on adsorption of the first pulse of carbon monoxide, dihydrogen was displaced/desorbed from the sample; with subsequent pulses of carbon monoxide no further dihydrogen displacement or evolution was detected. On thermal desorption only a small quantity of carbon dioxide was desorbed (6.6×10^{17} molecules CO_2 desorbed, $CO_{(ads.)} : CO_{2(des.)} = 8.8 : 1$) and no dihydrogen was detected.

The ^{14}C-carbon monoxide isotherm for Pt/silica, at 298 K, is presented in Fig. 3 (curve b). Evacuation of the catalyst for 0.5 h resulted in a loss of 47.4% of the adsorbed carbon monoxide. Admission of 6.67 kPa of ^{12}C-carbon monoxide to the evacuated system resulted in 90% removal of the ^{14}C-carbon monoxide remaining on the surface.

The infrared spectrum of carbon monoxide adsorbed on Pt/silica at 298 K, after subtraction of background, is shown in Fig. 4. The band is centered at 2085 cm^{-1} but has a slight shoulder on the high frequency side. On heating the sample the spectrum of adsorbed carbon monoxide had disappeared by 433 K.

Platinum/molybdena (I). The adsorption of carbon monoxide on Pt/molybdena (I) was measured at 294 and 273 K. The amount adsorbed, at both temperatures, was $(5.16 \pm 0.78) \times 10^{18}$ molecules g^{-1}, giving a CO : Pt ratio of 0.35 : 1.

Analysis during the adsorption revealed that no dihydrogen was displaced/desorbed from the catalyst on adsorption of carbon monoxide. On thermal desorption to 573 K only a small quantity of carbon dioxide was

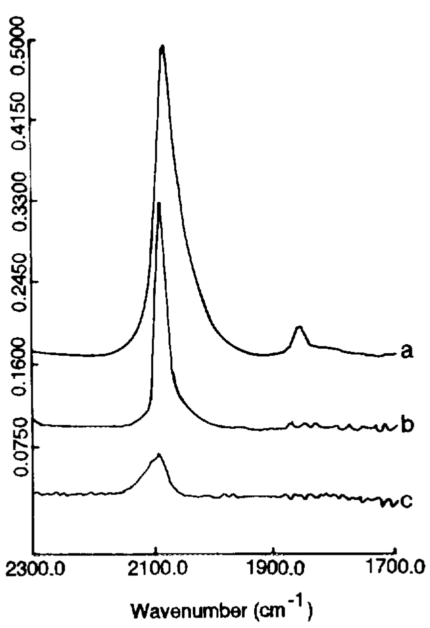

FIG. 4. FTIR spectra of carbon monoxide adsorbed on (a) Pt/alumina, (b) Pt/silica, and (c) Pt/molybdena (I).

desorbed (3.5×10^{17} molecules CO_2 desorbed, $CO_{(ads.)} : CO_{2(des.)} = 13.7 : 1$) and no dihydrogen was detected.

The ^{14}C-carbon monoxide isotherm for Pt/molybdena (I), constructed at 298 K, is presented in Fig. 3 (curve c). Evacuation of the saturated system for 0.5 h resulted in a loss of 68.0% of the adsorbed carbon monoxide. Subsequent admission of 6.67 kPa of ^{12}C-carbon monoxide to the evacuated system caused no change in the concentration of ^{14}C-carbon monoxide on the surface.

Carbon monoxide adsorption on Pt/MoO_3 (I) resulted in a broad asymmetric band in the infrared spectrum at 2088 cm^{-1} (Fig. 4). The spectrum of adsorbed carbon monoxide could still be detected on heating the sample to 546 K.

Platinum/molybdena (C). The adsorption of carbon monoxide on the Pt/molybdena (C) was studied at 273 K. The amount of CO adsorbed was $(1.23 \pm 0.15) \times 10^{18}$ molecules g^{-1}, giving a $CO_{(ads.)}$: Pt ratio of 0.08 : 1. On adsorption of the carbon monoxide no dihydrogen was displaced from the sample. On thermal desorption no quantifiable desorption of carbon monoxide occurred; however, at 573 K dihydrogen was desorbed.

No band in the infrared spectrum could be detected on adsorption of carbon monoxide on to Pt/molybdena (C).

The ^{14}C-carbon monoxide isotherm for Pt/molybdena (C), constructed at 298 K, is presented in Fig. 5. Evacuation of the saturated system for 16 h resulted in a loss of 46.5% of the adsorbed carbon monoxide. Subsequent admission of 6.67 kPa of ^{12}C-carbon monoxide to the evacuated system caused a 4.9% reduction in the concentration of ^{14}C-carbon monoxide on the surface.

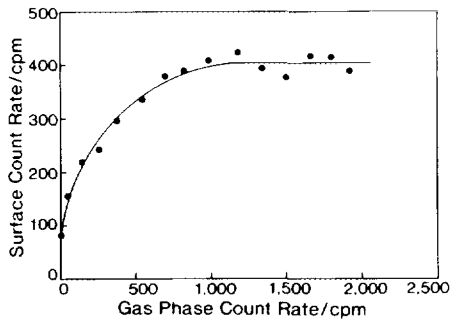

FIG. 5. ^{14}C-carbon monoxide adsorption isotherm obtained with Pt/molybdena (C) (0.204 g) at 294 K (^{14}CO specific activity = 0.203 mCi $mmol^{-1}$).

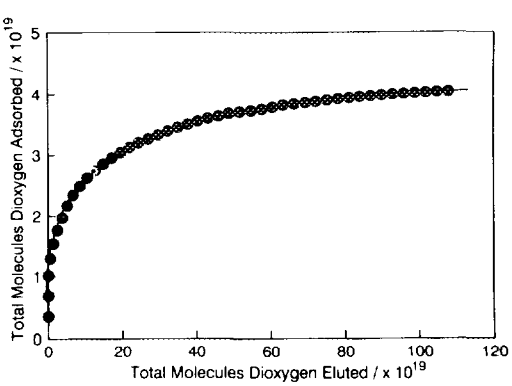

FIG. 6. Dioxygen adsorption isotherm obtained with Pt/molybdena (I).

Dioxygen Chemisorption

Platinum/alumina (I). The adsorption of dioxygen was studied by pulsing dioxygen over the catalyst, at 273 K, immediately after reduction. The amount adsorbed was $(6.81 \pm 0.15) \times 10^{18}$ molecules g^{-1}, giving an $O_{ads.}$: Pt ratio of 0.50 : 1.

Platinum/silica (I). The adsorption of dioxygen at 273 K was examined immediately after reduction; the amount adsorbed was 5.73×10^{18} molecules g^{-1}, giving an $O_{ads.}$: Pt ratio of 0.50 : 1.

Platinum/molybdena (I). Dioxygen was pulsed over the catalyst at 273 K immediately after reduction. However, both the amount of dioxygen adsorbed (4.052×10^{19} molecules g^{-1}, giving an $O_{ads.}$: Pt ratio of 5.53 : 1) and the shape of the isotherm (Fig. 6) suggested that the adsorption had involved not only the metal but also the support.

Platinum/molybdena (C). After reduction of a fresh sample dioxygen was pulsed over

TABLE 1

Adsorption of Carbon Monoxide and Dioxygen on the Various Catalysts

Catalyst	Temp.[a] (K)	Adsorbate	Amount adsorbed[b] (molecules × 10^{18})	X : Pt[c]
Pt/Al_2O_3 (I)	273	CO	19.79	0.72 : 1
Pt/Al_2O_3 (I)	273	O_2	6.81	0.50 : 1
Pt/SiO_2 (I)	256	CO	1.47	
Pt/SiO_2 (I)	273	CO	2.10	
Pt/SiO_2 (I)	273	CO	2.77	
Pt/SiO_2 (I)	294	CO	5.60	
Pt/SiO_2 (I)	273	O_2	5.73	0.50 : 1
Pt/MoO_3 (I)	273	CO	5.16	0.35 : 1
Pt/MoO_3 (I)	273	O_2	40.52	5.53 : 1
Pt/MoO_3 (C)	273	CO	1.23	0.08 : 1
Pt/MoO_3 (C)	273	O_2	0.00	0.00 : 1

[a] Temperature at which adsorption was measured.
[b] Units, molecules g^{-1}.
[c] X = CO or O dependent on adsorbing gas.

the catalyst at 273 K; no dioxygen adsorption was detected.

Table 1 summarises the carbon monoxide and dioxygen adsorptions for the four catalysts.

The Interaction of Carbon Monoxide and Dioxygen

Platinum/alumina (I). A sample was subjected to a series of six carbon monoxide adsorption–desorption cycles at 294 K as detailed above. No dihydrogen was liberated during adsorption after the fourth cycle; however, dihydrogen and carbon dioxide were both detected from each thermal desorption cycle. After the sixth adsorption/desorption cycle carbon monoxide was pulsed over the catalyst until saturation (1.108×10^{19} molecules g^{-1}). Once the catalyst was saturated with carbon monoxide, dioxygen was pulsed over the catalyst.

As dioxygen adsorbed, carbon dioxide was produced; the amount of carbon dioxide produced was equivalent to 91% of the carbon monoxide adsorbed on a molar basis. The amount of dioxygen adsorbed was 1.6×10^{18} molecules g^{-1}. On the assumption that the $CO_{(ads.)}$: Pt_s ratio was 1 : 1, then an $O_{(ads.)}$: Pt_s ratio of 0.32 : 1 was obtained. The catalyst was taken through a thermal desorption cycle; that is, it was heated to 573 K in flowing helium, cooled, and dioxygen pulsed over the sample until no further dioxygen adsorption took place. The amount of dioxygen adsorbed was 5.38×10^{18} molecules g^{-1} $O_{(ads.)}$: Pt = 0.39 : 1. Carbon monoxide was then pulsed over the dioxygen-saturated catalyst.

As carbon monoxide adsorbed, carbon dioxide was produced; 55% of the adsorbed dioxygen was removed as carbon dioxide (assuming $CO_{(ads.)} + 0.5O_{2(ads.)} \rightarrow CO_2$). The amount of carbon monoxide adsorbed was 1.318×10^{19} molecules g^{-1}. Coadsorbed carbon monoxide and dioxygen were now present on the sample and were stable at 293 K. When the catalyst was heated to 573 K in flowing helium, carbon dioxide desorbed ($CO_{(ads.)} : CO_{2(des.)} = 2.4 : 1$) but no dihydrogen desorbed. The amount of carbon dioxide produced accounted for the remaining 45% of the adsorbed dioxygen. The sample was subsequently cooled and a carbon monoxide adsorption/desorption cycle performed; there was coincident desorption of carbon dioxide and dihydrogen during the thermal desorption.

Platinum/silica (I). A Pt/silica catalyst was subjected to a series of four carbon monoxide adsorption–desorption cycles as detailed above. After the first cycle no dihydrogen was displaced/desorbed during adsorption; carbon monoxide and carbon dioxide were both detected from each thermal desorption cycle. After four adsorption/desorption cycles, carbon monoxide was pulsed over the catalyst until saturation (3.47×10^{18} molecules g^{-1}). Dioxygen was then pulsed over the carbon monoxide saturated sample.

As the dioxygen adsorbed, carbon dioxide was produced; the amount of carbon dioxide released was 7.13×10^{18} molecules g^{-1}. Therefore some of the carbon (monoxide) retained during the carbon monoxide adsorption/desorption cycles is also removed by dioxygen at 293 K. The amount of dioxygen adsorbed was 1.2 × 10^{18} molecules g^{-1}; assuming a $CO_{(ads.)}:Pt_s$ ratio of 1 : 1, then $O_{(ads.)}:Pt_s$ of 0.34 : 1 is obtained. When dioxygen adsorption had ceased the catalyst was heated to 573 K in flowing helium, cooled, and dioxygen pulsed over the sample until no further dioxygen adsorption was detected. The amount of dioxygen adsorbed was 4.73 × 10^{18} molecules g^{-1}, giving an $O_{(ads.)}:Pt$ ratio of 0.41 : 1. Carbon monoxide was then pulsed over the dioxygen-saturated catalyst. As the carbon monoxide adsorbed, carbon dioxide was produced; 70% of the adsorbed oxygen was removed as carbon dioxide and the catalyst adsorbed an enhanced amount of carbon monoxide, that is greater than that adsorbed on a fresh sample (7.07 × 10^{18} molecules g^{-1}, cf. 5.60 × 10^{18} molecules g^{-1}). Adsorbed carbon monoxide and dioxygen now coexisted and were stable at 293 K. The catalyst was heated to 573 K in flowing helium, when trace quantities of carbon monoxide and carbon dioxide were detected.

Platinum/molybdena (*I*). A catalyst was subjected to a series of four carbon monoxide adsorption–desorption cycles as detailed above. During adsorption of the carbon monoxide no dihydrogen was displaced/desorbed; carbon monoxide and carbon dioxide were both detected from each thermal desorption cycle.

After four adsorption/desorption cycles carbon monoxide was pulsed over the catalyst until saturation (2.22 × 10^{18} molecules g^{-1}). As dioxygen was pulsed over the saturated catalyst carbon *monoxide* was desorbed. This was in marked contrast to the behaviour of the Pt/alumina and Pt/silica catalysts, which both desorbed carbon *dioxide*. Approximately 25% (5.5 × 10^{17} molecules g^{-1}) of the initially adsorbed carbon monoxide was desorbed by dioxygen. The amount of dioxygen adsorbed was 1.435 × 10^{19} molecules g^{-1}, which gives an $O_{(ads.)}:Pt_s$ ratio of 1.9 : 1. The sample was heated to 573 K in flowing helium with the effluent passed through a trap at 77 K; no desorption products were detected. When dioxygen was preadsorbed no carbon monoxide adsorption occurred.

Platinum/molybdena (*C*). Due to the low carbon monoxide adsorption capacity and the absence of any detectable oxygen adsorption, no experiments similar to those described above were performed on this catalyst.

Effect of Retained Oxygen on Carbon Monoxide Adsorption

Platinum/alumina (*I*). Dioxygen was adsorbed on a fresh catalyst immediately after reduction. When adsorption ceased the gas flow was switched from helium to 5% dihydrogen/dinitrogen and the catalyst was held under this stream for 1 h, at 293 K. The carrier gas was then returned to helium and the sample heated to 573 K. A peak signifying dihydrogen desorption was detected, its maximum being at 390 K.

The sample was cooled to 273 K and carbon monoxide passed over the catalyst until saturation. The amount of carbon monoxide adsorbed was (1.515 ± 0.013) × 10^{19} molecules g^{-1}. When adsorption ceased the catalyst was heated to 573 K in flowing helium with the effluent being passed through a trap at 77 K. No carbon monoxide was desorbed from the catalyst. On warming the trap carbon dioxide was detected ($CO_{(ads.)}:CO_{2(des.)}$ = 2.1 : 1).

When the experiment was repeated using isotopically labelled carbon monoxide ($^{13}CO/C^{18}O$, 1 : 1), the desorbed carbon dioxide had an $^{18}O:{}^{16}O$ ratio of 0.02 : 1. This requires that 7.00 × 10^{18} oxygen atoms g^{-1} were left on the surface from the dioxygen adsorption, which is equivalent to 50% of that adsorbed. No isotope exchange in the carbon monoxide was detected.

Platinum/silica (*I*). Dioxygen was adsorbed on the catalyst immediately after reduction. When adsorption ceased the gas flow was switched from helium to 5% dihydrogen/dinitrogen. The catalyst was held under the 5% dihydrogen/dinitrogen stream for 1 h, at 293 K, whereupon the flow was switched to helium and the sample was heated to 573 K. A peak indicating dihydrogen desorption was detected, its maximum being at 378 K.

The sample was cooled to 294 K and isotopically labelled carbon monoxide ($^{13}CO/C^{18}O$, 1 : 1) passed over the catalyst until there was no further uptake. The amount of carbon monoxide adsorbed was 6.43×10^{18} molecules g^{-1}. During adsorption a trace of carbon dioxide was produced. Mass spectral analysis of the carbon dioxide revealed that although the $^{12}C : ^{13}C$ ratio was the same as in the starting carbon monoxide, the $^{18}O : ^{16}O$ ratio had altered from 1.4 : 1 in the starting carbon monoxide to 0.3 : 1 in the exit carbon dioxide. When adsorption had ceased the catalyst was heated to 573 K in flowing helium, with the effluent gas being passed through a trap at 77 K. No carbon monoxide was desorbed from the catalyst. On warming the trap carbon dioxide was detected ($CO_{(ads.)} : CO_{2(des.)}$ = 14.8 : 1).

Platinum/molybdena (1). Dioxygen was adsorbed on the catalyst as described above. When adsorption ceased the gas flow was switched from helium to 5% dihydrogen/dinitrogen. The catalyst was subjected to the 5% dihydrogen/dinitrogen stream for 1 h at 293 K, then the gas flow was returned to helium and the sample heated to 573 K. A dihydrogen desorption peak was detected with the peak maximum at 373 K. At 493 K the sample again began to evolve dihydrogen and this continued until heating was stopped at 573 K. The sample was then cooled to 273 K and carbon monoxide passed over the catalyst until there was no further uptake. The amount of carbon monoxide adsorbed was 2.86×10^{18} molecules g^{-1}. When adsorption ceased the catalyst was heated to 573 K in flowing helium with the effluent gas being passed through a trap at 77 K. Only a trace of carbon monoxide was desorbed from the catalyst during thermal desorption. On warming the trap, carbon dioxide was detected ($CO_{(ads.)} : CO_{2(des.)}$ = 16.8 : 1).

Platinum/molybdena (C). Dioxygen was passed over the catalyst sample as outlined in the dioxygen adsorption section. No adsorption was observed; the helium gas flow was switched to 5% dihydrogen/dinitrogen for 1 h at 293 K, then returned to helium and the sample heated to 573 K. At 493 K dihydrogen evolution commenced and continued until heating was stopped at 573 K.

The sample was cooled to 273 K and carbon monoxide passed over the catalyst until there was no further uptake. The amount of carbon monoxide adsorbed was 2.5×10^{17} molecules g^{-1}. On thermal desorption to 573 K no detectable amount of carbon monoxide or dioxide was desorbed. Dihydrogen was again desorbed with maximum rate of desorption occurring at 573 K.

DISCUSSION

Carbon Monoxide Adsorption

Platinum/alumina (1). The adsorption of carbon monoxide on platinum/alumina catalysts is a system which has been well studied (*4–10*) and in general our results are in agreement with the literature. ^{14}C-carbon monoxide chemisorption indicates that there are two forms of adsorbed carbon monoxide distinguishable by their strength of adsorption. There is a weakly bound species which can be reasonably assumed to give rise to the secondary adsorption which is removable by evacuation. Such a secondary adsorption is unusual with carbon monoxide adsorption over Group VIII metals (*11*), but similar observations have been obtained for carbon monoxide adsorption on copper in a partially oxidised state (*12*), and a weakly held adsorbed state of carbon monoxide has also been observed on Pt/alumina by Bain *et al.* (*4*) and by Heyne and Tompkins (*5*). Bain *et al.* (*4*) report that the amount weakly held was 35%, which is in reasonable agreement with our figure of 27%. The primary region of the isotherm is typical of strong carbon monoxide adsorption on platinum that is not removable by evacuation.

Adsorbed carbon monoxide which is stable *in vacuo* at 298 K (i.e., the primary region of the isotherm) gives an infrared spectrum that indicates that there are two species present, one linear (2076 cm^{-1}) and one bridged (1857 cm^{-1}), with the majority species being linearly bound. This agrees with Primet *et al.* (*6*), who reported bands at 2075 and 1850 cm^{-1}. From the adsorption measurements using ^{14}C-carbon monoxide, 84% of the strongly adsorbed species is exchangeable with gas phase carbon monoxide. Therefore it is the linearly bound form of adsorbed carbon monoxide which exchanges with the gas phase.

When carbon monoxide is pulsed over platinum/alumina in a flow of helium the adsorbed species can be equated with the strongly bound species detectable by infrared spectroscopy and static ^{14}C-carbon monoxide chemisorption. From the initial pulse-flow carbon monoxide chemisorption results, and assuming a linearly bound species with a 1 : 1 $CO_{ads.}$: Pt_s ratio, a platinum particle size of ~2.5 nm can be calculated, which is not inconsistent with that obtained from electron microscopy, as discussed in Part I (*1*).

Adsorption of the first pulse of carbon monoxide on the Pt/alumina catalyst results in no displacement of dihydrogen indicating that the reduction procedure does not leave residual hydrogen upon the surface. However, upon adsorption of the second and third pulses of carbon monoxide, dihydrogen was desorbed, and this process was repeatable throughout four adsorption/thermal desorption cycles. Subsequent carbon monoxide adsorptions resulted in no dihydrogen being desorbed. Therefore, there is a limited quantity of hydrogen which is not initially on the surface but can be liberated on adsorption of carbon monoxide. Paál and Thomson (*13, 14*) showed that both supported platinum and platinum black can absorb hydrogen, hence a limited amount of hydrogen can be present inside platinum crystallites; in addition, Wells has proposed "hydrogen occlusion" as a general phenomenon (*15*) with Group VIII metals. However, it is difficult to assign such behaviour to this catalyst given the small size of the platinum crystallites (*1*). Norton *et al.* (*16*) have shown that adsorption of carbon monoxide on Pt(110) results in a surface reconstruction which also affects subsurface layers, whilst Christmann and Ertl (*17, 18*) have shown that H-atoms prefer binding to a highly coordinated site and that these atoms have a higher average heat of adsorption (by 10 kJ mol^{-1}) than those adsorbed on lower coordination sites. Therefore, the adsorption of the first pulse of carbon monoxide can result in a surface reconstruction/relaxation which can lower the heat of adsorption for the H-atoms by several kJ mol^{-1} and hence make them susceptible to displacement by further pulses of carbon monoxide. Further evidence supporting this interpretation will be forthcoming in a following paper which deals with the coadsorption of carbon monoxide and ethene.

On thermal desorption, carbon monoxide, carbon dioxide and dihydrogen were all detected in the reactor effluent. Carbon dioxide and dihydrogen were found to have coincident desorption temperatures which usually indicates that they are desorption products from a common species (*19*); however, in this case, this is unlikely. Clearly, the carbon dioxide is formed from carbon monoxide by addition of an oxygen atom but, as is reported elsewhere in this paper, a reaction

$$CO(ads) + O(ads) \rightarrow CO_2(g)$$

results in no coincident evolution of dihydrogen. Therefore a simple oxidation or the conversion

$$2CO(ads) \rightarrow CO_2(g) + C(ads)$$

can be discounted. To achieve coincident desorption, hydrogen must be involved in the process at the surface. As this process occurs even after all the strongly bound hydrogen has been removed and the only substantial source of hydrogen in the catalyst is the population of hydroxyl groups on the support, then a reaction of the type

$$\mathrm{CO(ads)} + \mathrm{OH(support)} \rightarrow \mathrm{CO_2(g)} + 0.5\mathrm{H_2(g)}$$

is likely at the metal–support interface and would result in coincident desorption of carbon dioxide and dihydrogen. It is possible that the secondary adsorption region found at low temperatures in a static system may be due to carbon monoxide adsorbed at the interface, but below the temperature at which reaction is initiated.

In summary, three states of adsorbed carbon monoxide have been detected, one weakly held at 293 K and two strongly held. Of the two strongly adsorbed states, one is linearly bonded, the other bridge bonded. Approximately 84% of the strongly held material is able to exchange with gas phase carbon monoxide. Adsorption of submonolayer levels of carbon monoxide results in a surface process which modifies the strength of binding of surface hydrogen such that subsequently it can be displaced by carbon monoxide. Carbon monoxide reacts with surface hydroxyls during thermal desorption to form carbon dioxide and dihydrogen.

Platinum/silica (*1*). The ^{14}C-carbon monoxide adsorption isotherm obtained with the Pt/silica catalyst also exhibited primary and secondary regions in the isotherm with the species responsible for the secondary region only weakly adsorbed. Bain *et al.* (*4*) also detected a weakly bound species similar to that found with Pt/alumina on Pt/silica. The strongly adsorbed species exchanged with gas-phase carbon monoxide to the extent of 90%. The infrared analysis of the adsorbed species giving rise to the primary region showed only one band indicative of linearly bound carbon monoxide (2085 cm^{-1}), which is in good agreement with that obtained by Sarkany and Gonzalez (*20*) at 2083 cm^{-1}. The results from the EUROPT-1 study (*21*) differ in that three bands are recorded, with the highest being at 2075 cm^{-1}; however, at high coverages one of the participating laboratories obtained a band at 2080 cm^{-1}. These results are in keeping with those obtained from the Pt/alumina catalyst; however, the pulse chemisorption revealed some differences. Carbon monoxide adsorption on platinum is not, under normal conditions, considered to be an activated process, yet with this catalyst an activation barrier to adsorption was observed. However, with this catalyst, there is some residual surface hydrogen which is displaced by incoming carbon monoxide. If the strength of the M–H bond was similar to that of the M–CO bond, then the observed effect on the carbon monoxide adsorption would be an activated adsorption and indeed, on Ru(0001), evidence has been obtained for adsorbed H-atoms hindering subsequent carbon monoxide adsorption (*22*).

In summary, three types of adsorbed species have been detected: (i) a weakly bound state removeable by pumping at 293 K, and (ii) two strongly bound states, one of which exchanges with gas phase carbon monoxide and is linearly bonded, and a second which does not exchange and which represents less than 10% of the strongly adsorbed material. The catalyst retains surface hydrogen which may be responsible for the apparent activation energy barrier observed in carbon monoxide adsorption.

Platinum/molybdena (*1*). The ^{14}C-carbon monoxide adsorption isotherm showed both a primary and secondary adsorption region although, because of the small uptake, they are not well defined. The secondary region was again removable by evacuation; however, no exchange with gas phase carbon monoxide was detected for the species which makes up the primary region, which contrasts with the behaviour observed with both the silica- and alumina-supported samples. However, given the small uptake, coupled with the inherent standard deviation encountered in the radiotracer counting statistics, it is possible that a small degree of exchange may have gone undetected. The infrared spectrum of material adsorbed in the primary region exhibited a single band (2088 cm^{-1}) assigned to linearly bound carbon monoxide. Therefore all the linearly bound species are (within experimental error) nonexchangeable, whereas, with the silica- and the alumina-supported samples, a significant proportion of the linearly bonded species was exchangeable. Therefore, either there are no adsorption sites available for incoming gas molecules, that is,

$$CO(g) \not\rightarrow CO(ads.),$$

or there must be no equivalence of the newly adsorbed molecule with the species already present on the surface, that is,

$$CO(g) \rightarrow CO(ads.) \not\rightarrow {}^*CO(ads.).$$

Thus on the Pt/molybdena (I) catalyst there are only two detectable adsorbed states of carbon monoxide, compared to three on the Pt/alumina and Pt/silica. Of these two, the strongly adsorbed state, although linearly bound, does not exchange with gas-phase carbon monoxide, in contrast to the situation on Pt/alumina and Pt/silica where over 80% of this species was exchangeable.

Platinum/molybdena (C). Static adsorption using ^{14}C-carbon monoxide showed there to be primary and secondary adsorption regions and that only a small proportion (approx. 5%) of the material corresponding to the primary region was exchangeable. This suggests that the catalyst is similar to the one prepared by impregnation, although there are significant differences. Of all our catalysts, this sample exhibits the lowest capacity for carbon monoxide adsorption, possibly due to platinum being trapped in the bulk and not available to participate in adsorption; also, no band for adsorbed carbon monoxide was detected in the infrared spectrum after adsorption. However, the absence of a band may be ascribed to a lack of sensitivity since the amount of carbon monoxide adsorbed (as determined from the pulse-flow measurements) was not sufficient to guarantee infrared detection in the diffuse reflectance mode.

Therefore on Pt/molybdena (C), three adsorbed states of carbon monoxide are detected. One is a weakly bound species and two are strongly bound, one of which can exchange with gas-phase carbon monoxide to the extent of 5%.

Dioxygen Chemisorption

Platinum/alumina (I), Pt/silica (I). Dioxygen adsorption over the alumina- and silica-supported samples showed no unique features. However, it is noticeable that the $O_{(ads.)}$: Pt ratios are similar, indicating a similar degree of dispersion. The value of 0.5 : 1 obtained with these two catalysts is consistent with the adsorption of dioxygen on small platinum particles as previously proposed by Wilson and Hall (*23*). The results are also in agreement with the electron microscopy results quoted in Part I (*1*), which indicated that the alumina- and silica-supported catalysts have similar particle size distributions. With the alumina-supported sample the extent of dioxygen adsorption is not approximately half the extent of carbon monoxide adsorption, as would be expected (i) if the dioxygen adsorbed in a random two-site manner, (ii) given that the majority of the carbon monoxide is adsorbed linearly, and (iii) remembering that a 1 : 1 $CO_{(ads.)}$: Pt_s and $O_{(ads.)}$: Pt_s was obtained for EUROPT-1 (*21*). However, Norton *et al.* (*16*) have determined the absolute coverages of carbon monoxide and oxygen on Pt(111) and have compared carbon monoxide coverages on Pt(100), Pt(110), and Pt(111) and have found them to be within 6% of each other. At 300 K on Pt(111) the ratio between the number of adsorbed oxygen atoms and the number of adsorbed carbon monoxide molecules is 0.53, not 1; on this basis, an adsorption of 1.979×10^{19} carbon monoxide molecules on Pt/alumina should result in an oxygen atom adsorption of 1.043×10^{19}, which is in reasonable agreement with our value of 1.362×10^{19}.

Platinum/molybdena (C). The absence of dioxygen adsorption on this catalyst is highly unusual. When the sample was reduced the molybdenum trioxide was converted into a hydrogen bronze as outlined in the previous paper (*1*). Such material normally adsorbs dioxygen; however, the absence of bulk oxidation of the support indicates that oxidation of the hydrogen molybdenum bronze requires adsorption and subsequent spillover from the metal to the support rather than direct adsorption on the support from the gas phase.

Platinum/molybdena (*1*). Dioxygen adsorption on a sample of the Pt/molybdena bronze is complicated by adsorption on the support. Hence, the measured uptake is that on both the support and the metal. Even assuming that all the dioxygen is chemisorbed on the support, the total quantity is insufficient to fully reoxidise the molybdena bronze, in agreement with the XPS results presented in Part I (*1*).

The Interaction of Carbon Monoxide and Dioxygen

Platinum/alumina (*1*). When dioxygen was pulsed over a carbon monoxide precovered surface there was immediate production of carbon dioxide, which continued until most of the carbon monoxide had been removed. However, not all of the adsorbed carbon monoxide reacted, approximately 9% being unreactive to adsorbed oxygen at 293 K.

Two strongly bound species of carbon monoxide have been shown to be present on the surface and the one which did not undergo ($^{12}CO/^{14}CO$) exchange constituted approximately 16% of the total adsorbed. Given the difference in techniques used to obtain the two measurements, it is likely that the species which does not undergo exchange is also that which is unreactive to oxygen at 293 K.

When an oxygen precovered surface was subjected to pulses of carbon monoxide only 55% of the adsorbed oxygen was reactive at 293 K, so that 4.84×10^{18} oxygen atoms g^{-1} were retained by the catalyst. This difference in behaviour between carbon monoxide reacting with an oxygen precovered surface and oxygen reacting with a carbon monoxide precovered surface has been observed previously (*24*).

On heating the catalyst the retained oxygen was removed by reaction with adsorbed carbon monoxide to give carbon dioxide, with no coincident evolution of dihydrogen. When a carbon monoxide chemisorption was carried out immediately after this series of reactions there was, on thermal desorption, coincident desorption of carbon dioxide and dihydrogen. This confirms that carbon dioxide can be produced from an oxygen/carbon monoxide reaction with no desorption of dihydrogen and that there is another process for the production of carbon dioxide which results in coincident desorption of carbon dioxide and dihydrogen, that is,

$$\mathrm{CO(ads)} + \mathrm{OH(support)} \rightarrow \mathrm{CO_2(g)} + 0.5\mathrm{H_2(g)}.$$

Platinum/silica (*1*). The reaction observed when dioxygen was pulsed over a carbon monoxide precovered Pt/silica sample was similar to that found with Pt/alumina; however, the reaction was more facile and some of the retained species present after the four adsorption/desorption cycles was also oxidised. This indicates a higher reactivity for this catalyst than has been reported in the literature (*24*). However, the ratio obtained of oxygen atoms adsorbed to the number of sites liberated by the oxygen treatment is 0.34, which agrees with the value of 0.32 obtained for the Pt/alumina catalyst, indicating a similarity in adsorbed state.

When carbon monoxide was pulsed over an oxygen precovered Pt/silica, 70% of the adsorbed oxygen was removed, again indicating a higher activity than for Pt/alumina. On subsequent adsorption of carbon monoxide, the sample adsorbed 26% more carbon monoxide than a fresh catalyst. This unusual result may be caused either by surface restructuring or by a reduction in the activation energy barrier which exists for carbon monoxide adsorption on this sample. Reduction of this barrier may be achieved by the preadsorbed dioxygen removing the residual hydrogen left after the reduction process and proposed (above) to be responsible for the activation of the carbon monoxide adsorption.

Platinum/molybdena (I). When dioxygen was passed over a sample precovered with carbon monoxide, desorption of carbon monoxide occured and no carbon dioxide was formed. This unusual result is in keeping with the behaviour of the catalyst towards carbon monoxide adsorption. For both the Pt/silica and Pt/alumina catalysts, the amount of carbon dioxide produced is related to the amount of exchangeable carbon monoxide as detected in the $^{14}C/^{12}C$-carbon monoxide exchange reaction. However, no adsorbed carbon monoxide could be exchanged on the Pt/molybdena catalyst and hence there is no carbon dioxide production. The amount of adsorbed dioxygen is also reduced from that adsorbed on a fresh catalyst, indicating that the route for oxygen transfer to the support is via the metal and is hindered by the presence of the carbon monoxide. This is consistent with the XPS results presented in Part I (*1*), which indicated that no Mo(V) state was present, as it is this valency state which would be expected to participate in the direct adsorption of dioxygen.

Effect of Residual Dioxygen on Carbon Monoxide Adsorption

Platinum/alumina (I). After adsorption of dioxygen at 293 K, treatment of the catalyst with 5% dihydrogen/dinitrogen does not totally re-reduce the surface. Dihydrogen is adsorbed yet does not undergo reaction with all the adsorbed oxygen. This behaviour is similar to that seen with carbon monoxide pulsed over an oxygen precovered surface. Using isotopically labelled gases, the amount of residual oxygen has been determined to be 7×10^{18} oxygen atoms g^{-1}, which is greater than the amount of oxygen (4.84×10^{18} oxygen atoms g^{-1}) which did not react with carbon monoxide pulsed over an oxygen precovered sample. In fact the reactivity of adsorbed oxygen to both hydrogen and carbon monoxide is very similar but with carbon monoxide, as expected, being the stronger reducing agent. The nonreacting hydrogen subsequently desorbs as dihydrogen. Carbon monoxide adsorption on the catalyst after this treatment is reduced by 23.5%, probably due to site blocking by residual oxygen adatoms, and during thermal desorption there is an increase in the amount of carbon dioxide produced due to

$$CO(ads.) + 0.5O_2(ads.) \rightarrow CO_2$$

(note no coincident dihydrogen desorption).

Platinum/silica (I). The Pt/silica catalyst behaves in qualitatively the same way as the Pt/alumina and the same arguments apply, although the amount of carbon monoxide adsorbed (6.43×10^{18} molecules g^{-1}) is higher than that adsorbed on a fresh catalyst at 294 K (see Table 1). As outlined previously, this enhancement of adsorptive capacity appears to require that either oxygen is present, or that the catalyst has been treated with oxygen, resulting in a surface restructuring or a reduction in the activation energy barrier which exists for carbon monoxide adsorption on this catalyst.

Platinum/molybdena (I). This Pt/molybdena is significantly different from the other catalysts. Treatment with dihydrogen at 293 K after dioxygen adsorption is sufficient to regenerate the hydrogen molybdenum bronze. The catalyst desorbs dihydrogen at a temperature similar to that observed for the other catalyst samples, but there is then a continuous evolution of dihydrogen due to reverse spillover from the hydrogen molybdenum bronze. The reduced amount of carbon monoxide adsorption (45%) is in keeping with the other catalysts and is related to the presence of residual oxygen on the surface; however, because of oxygen spillover to the support, dioxygen adsorption on the metal component was not quantifiable.

Platinum/molybdena (C). After treatment with dihydrogen at 293 K there was no subsequent detectable desorption of dihydrogen which could be associated solely with the metal component of the catalyst. However, the formation of the hydrogen molybdenum bronze and the subsequent desorption of dihydrogen indicates that there is metal available for dihydrogen/hydrogen, adsorption/desorption, dissociation/association, and spillover/reverse spillover. The loss of 80% of the carbon monoxide chemisorption capacity suggests that either residual hydrogen was blocking the adsorption or that there was some limited dioxygen adsorption which was below the limit of detection and did not spillover onto the hydrogen molybdenum bronze.

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REFERENCES

1. Jackson, S. D., Keegan, M. B. T., McLellan, G. D., Moyes, R. B., Simpson, S., Webb, G., Wells, P. B., Whyman, R., and Willis, J., *J. Catal.*, in press.
2. Al-Ammar, A. S., and Webb, G., *J. Chem. Soc. Faraday Trans. 1* **74,** 175 (1978).
3. Moon, S. H., Windawi, H., and Katzer, J. R., *Ind. Eng. Chem. Fundam.* **20,** 396 (1981).
4. Bain, F. T., Jackson, S. D., Thomson, S. J., Webb, G., and Willocks, E., *J. Chem. Soc. Faraday Trans. 1* **72,** 2516 (1976).
5. Heyne, H., and Tompkins, F. C., *Trans. Faraday Soc.* **63,** 1274 (1967).
6. Primet, M., Basset, J. M., Mathieu, M. V., and Prettre, M., *J. Catal.* **29,** 213 (1973).
7. Apesteguia, C. R., Garetto, T. F., and Borgna, A., *J. Catal.* **106,** 73 (1987).
8. Venus, D., Hensley, D. A., and Kesmodel, L. L., *Surf. Sci.* **199,** 391 (1988).
9. Eischens, R. P., and Pliskin, W. A., *in* "Advances in Catalysis" (D. D. Eley, W. E. Frankenburg, and V. I. Komoreusky, Eds.), Vol. 10, p. 2. Academic Press, New York, 1958.
10. Sarkany, J., and Gonzalez, R. D., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 548 (1983).
11. Berndt, G. F., Thomson, S. J., and Webb, G., *J. Chem. Soc. Faraday Trans. 1* **79,** 195 (1983).
12. Kinnaird, S., Webb, G., and Chinchen, G. C., *J. Chem. Soc. Faraday Trans. 1* **83,** 3399 (1987).
13. Paál, Z., and Thomson, S. J., *Radiochem. Radioanal. Lett.* **12,** 1 (1972).
14. Paál, Z., and Thomson, S. J., *J. Catal.* **30,** 96 (1973).
15. Wells, P. B., *J. Catal.* **52,** 498 (1978).
16. Norton, P. R., Davies, J. A., Creber, D. K., Sitter, C. W., and Jackman, T. E., *Surf. Sci.* **108,** 205 (1981).
17. Christmann, K. R., and Ertl, G., *Surf. Sci.* **60,** 365 (1976).
18. Christmann, K. R., *in* "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 3. Marcel Dekker, New York, 1988, and references therein.
19. Madix, R. J., and Wachs, I. E., *J. Catal.* **53,** 208 (1978); Bowker, M., Houghton, H., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **83,** 3023 (1981).
20. Sarkany, J., and Gonzalez, R. D., *Appl. Catal.* **4,** 53 (1982).
21. Wells, P. B., *Appl. Catal.* **18,** 259 (1985).
22. Peebles, D. E., Schreifels, J. A., and White, J. M., *Surf. Sci.* **116,** 117 (1982).
23. Wilson, G. R., and Hall, W. K., *J. Catal.* **17,** 190 (1970).
24. Bennett, C. O., Laporta, L. M., and Cutlip, M. B., *in* "Studies in Surface Science and Catalysis" (A. Crucq and A. Frennet, Eds.), Vol. 30, p. 143. Elsevier, Amsterdam, 1987.