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The Stoichiometry of Hydrogen and CO Chemisorption on Ir/γ-Al_2O_3

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The stoichiometry of hydrogen and carbon monoxide chemisorption on Ir/γ-Al_2O_3 was examined at metal loadings of 0.2–1.0 wt%. Using temperature programmed desorption (TPD), up to two atoms of hydrogen were found to be chemisorbed per iridium atom. This is in agreement with CO adsorption results which indicated the chemisorption of up to two CO molecules per iridium atom. The TPD of hydrogen followed second-order kinetics indicating that chemisorption occurs dissociatively upon iridium. The activation energy for desorption of hydrogen was found to be in the range of 11–17 kcal/g mol.

INTRODUCTION

There has been a recent interest in characterizing iridium on inorganic oxide supports by chemisorption. This is due to the difficulty in applying X-ray diffraction and electron microscopy techniques, especially when the metals are highly dispersed.

Several investigators have reported the chemisorption of hydrogen and carbon monoxide on iridium (*1–3*). In calculating dispersions these authors have assumed a stoichiometry of one hydrogen atom or one CO molecule per iridium atom. This is based on the observed stoichiometry of one of its closest neighbors in the periodic table, namely, platinum. Sinfelt and co-workers (*4, 5*) have examined the hydrogen and CO chemisorption on supported Pt, Ir, and Pt–Ir. The above authors found that in the case of Ir and Pt–Ir, adsorption stoichiometries could be in excess of one, for the above gases, especially at low metal loadings. Recently, McVicker *et al.* (*6*) have reported a stoichiometry of H/Ir = CO/Ir = 2 for highly dispersed Ir/η-Al_2O_3.

Very little information is available in the literature on the temperature programmed desorption (TPD) of hydrogen from iridium at low metal loadings. Mimeault and Hansen (*7*) found the flash desorption of hydrogen from unsupported iridium to follow second-order kinetics with an activation energy of 23.9 kcal/g mol. The desorption spectrum indicated two distinct peaks at 7 and 177°C, respectively. Contour and Pannetier (*8*) observed two peaks at 150 and 575°C in the hydrogen TPD spectrum of a 36 wt% Ir/γ-Al_2O_3. The enthalpies of adsorption were reported to be 10.3 and 27 kcal/g mol, respectively.

Escard *et al.* (*9*) obtained four peaks at −50, 50, 120, and 500°C in the hydrogen TPD spectrum of a 36 wt% Ir/η-Al_2O_3. The desorptions were found to be second order with activation energies of 6.45, 9.1, 10.5, and 25.1 kcal/g mol. The peak at 120°C was not found on unsupported iridium.

Rasser (*10*) investigated the TPD of hydrogen from Pt–Ir catalysts of various compositions and impregnated on various supports, ie., SiO_2, α-Al_2O_3, γ-Al_2O_3. Seven different adsorbed species for iridium, five of them irreversible at room temperature, were reported.

We report here the results from an investigation of the TPD of hydrogen from Ir/γ-Al_2O_3 at metal loadings of 0.2–1.0 wt%. The stoichiometry of chemisorption, as well as the order and activation energy of

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desorption were determined. CO adsorption was also performed to confirm the results from the TPD of hydrogen.

EXPERIMENTAL

Preparation of Ir/γ-Al_2O_3. The catalyst samples were prepared by incipient wetness impregnation of γ-Al_2O_3 with an aqueous solution of hexachloroiridic acid. The freshly impregnated catalysts were dried in air for 16 hours at 110°C and then calcined at 250°C in dry air for 4 hours. The iridium loadings were 0.26, 0.48, 0.56, and 0.95 (*11*). The γ-Al_2O_3 support had a BET surface area of 202 m^2/g.

Apparatus. The TPD of hydrogen and CO adsorption experiments were performed in the set-up shown in Fig. 1. It consisted of a sample holder of known volume that could be enclosed in a furnace and heated up to 600°C. The sample chamber could be evacuated to 10^{-5} Torr as measured by a Granville Phillips, Series 270 ionization gauge. Such a high vacuum was attainable through a series of oil and Hg diffusion pumps. Data acquisition and control were accomplished with a Hewlett Packard 9835A minicomputer. The CO adsorption experiments were initiated by reducing the sample in hydrogen at 450°C for a half hour and then evacuating the sample. After cooling the sample to room temperature the adsorption isotherm was obtained in the following manner. The section of tubing between valves V1 and V2, of known volume, was filled with CO to a desired pressure, which could be measured accurately using an MKS-5A Baratron capacitance manometer. The sample was exposed to known volumes of adsorbate via valve V2. The gas uptake at each pressure was measured after allowing a half hour for equilibration. Dispersion was calculated by extrapolating the adsorption isotherm to zero pressure and assuming the CO uptake at this pressure to correspond to monolayer coverage of the metal. In calculating dispersions from CO uptake, linear bonding of the CO molecule to iridium was assumed (*6*).

The TPD experiments were performed according to the time temperature profile shown in Fig. 2. The sample was initially reduced in hydrogen at 450°C for a half hour. This was followed by cooling to room temperature and then evacuation for a half hour. The desorption of hydrogen was then initiated at a chosen programming rate and the desorbed hydrogen collected in vessel B1 of known volume (Fig. 1). This was accomplished by using the oil and Hg diffu-

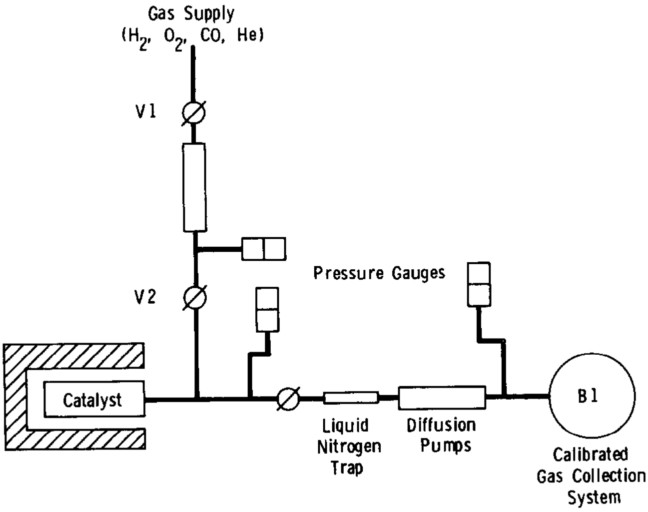

FIG. 1. Experimental setup.

sion pumps to effectively sweep the desorbed hydrogen from the sample chamber into the constant volume collection system. By monitoring the pressure of the gas in vessel B1, using an MKS-5A Baratron capacitance manometer, the rate of change of pressure with temperature, i.e., the desorption spectrum can be obtained. The dispersion can then be calculated for a given stoichiometry by integrating the area under the relevant desorption curve. This method was found to provide reproducible results.

Purity of gases. In house hydrogen was prepurified to <1 ppm of O_2 and H_2O by passing it through a Matheson Deoxo unit followed by a 13× molecular sieve drier. Research grade (Matheson 99.99%) CO was used directly from a lecture bottle.

MATHEMATICAL ANALYSIS

The order and activation energy of desorption can be determined by the following mathematical analysis of the TPD profiles. The following *N*th order kinetic expression can be used to describe the desorption of a given adsorbate from a given metal if

(1) a uniform surface exists with identical adsorption sites;

(2) there is negligible interaction between the adsorbed molecules on the surface;

(3) the molecular form of the adsorbate is the same as that of the gas.

$$-\frac{dn_a}{dt} = k_{do}\, n_a^N \exp\left[-\frac{E_d}{RT}\right]. \tag{1}$$

For a linear program given by $T = \alpha + \beta t$, where β is the heating rate in °C/min, the above equation can be rewritten as

$$-\frac{dn_a}{dT} = \frac{k_{do}}{\beta}\, n_a^N \exp\left[-\frac{E_d}{RT}\right]. \tag{2}$$

For small changes in n_a and T, Eq. (2) can be rewritten as

$$\frac{-\Delta n_a}{\Delta T} = \frac{k_{do}}{\beta}\, n_a^N \exp\left[-\frac{E_d}{RT}\right]; \tag{3}$$

rearranging Eq. (3)

$$\ln\left[-\frac{1}{n_a^N}\frac{\Delta n_a}{\Delta T}\right] = \ln\left[\frac{k_{do}}{\beta}\right] - \frac{E_d}{RT}. \tag{4}$$

The order of desorption then, is that value of N for which a plot of

$$\ln\left[-\frac{1}{n_a^N}\frac{\Delta n_a}{\Delta T}\right] \text{ vs } \frac{1}{T}$$

yields a straight line with a slope of $-E_d/R$.

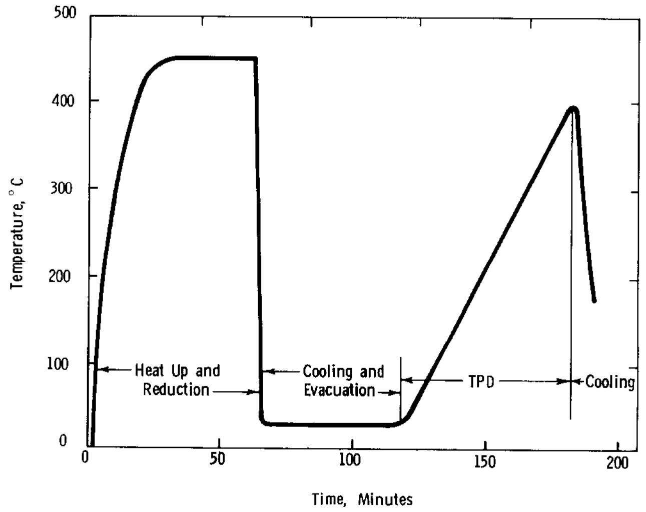

FIG. 2. Temperature vs time history for a typical TPD experiment.

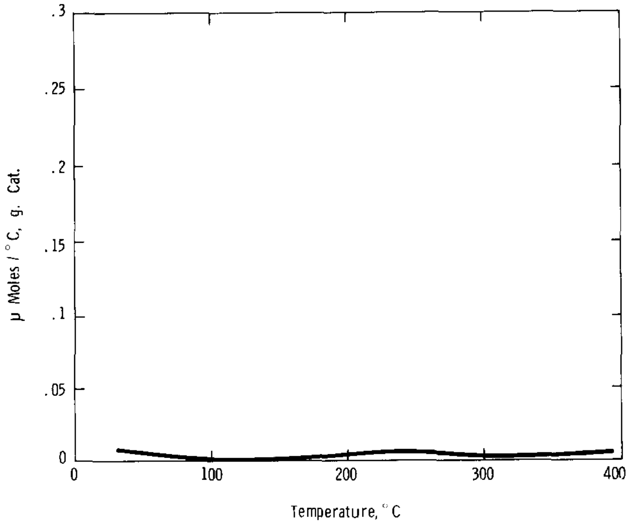

FIG. 3. Desorption spectrum for 0.6 wt% Ir/γ-Al_2O_3 sintered in air at 600°C.

The activation energy can also be calculated from the temperature at which dn_a/dT is maximum in the following manner. Such a maximum occurs at a temperature $T_{\max}$ where $d/dT(dn_a/dT) = 0$. Taking the derivative of Eq. (2) with respect to T and setting it to zero we get

$$\frac{n_a E_d}{RT^2}\bigg|_{\max} - N\left(-\frac{dn_a}{dT}\right)\bigg|_{\max} = 0. \tag{5}$$

Rearranging Eq. (5)

$$\frac{E_d}{RT^2}\bigg|_{\max} = \frac{N(-dn_a/dT)}{n_a}\bigg|_{\max} \tag{6}$$

RESULTS AND DISCUSSION

Preliminary Experiments

In order to confirm the origin of the peaks in the desorption spectrum, a 0.6 wt% sample was sintered by exposing it to air at 600°C for 6 hr. The desorption spectrum of this sample, shown in Fig. 3, indicates that the peaks occurring in the temperature range of 25–400°C are only due to dispersed iridium.

The desorption of a chemisorbate is often effected using a linear program in the range of 5–20°C. In order to select an optimum programming rate for the present study, the desorption spectrum of a 0.6 wt% Ir/γ-Al_2O_3 was examined at rates of 5, 10, and 15°C/min. The results shown in Fig. 4 indicate that the position in the primary peak at 150°C is not affected by the programming rate. Diffusional effects are therefore unimportant at these rates. A rate of 5°C/min was chosen as it permitted maximum resolution of the peaks in the desorption spectra.

TABLE 1

Hydrogen Chemisorption on Ir/γ-Al_2O_3

Number	Ir loading wt%	H/Ir molar ratio	
		Area 1	Area 2
1	0.26	0.22	2.2
2		0.22	2.22
3	0.48	0.24	2.26
4		0.28	2.44
5	0.56	0.58	1.92
6		0.48	2.14
7		0.58	1.86
8		0.54	1.70
9	0.95	—	(1.44)
10		—	(1.56)
11		—	(1.58)

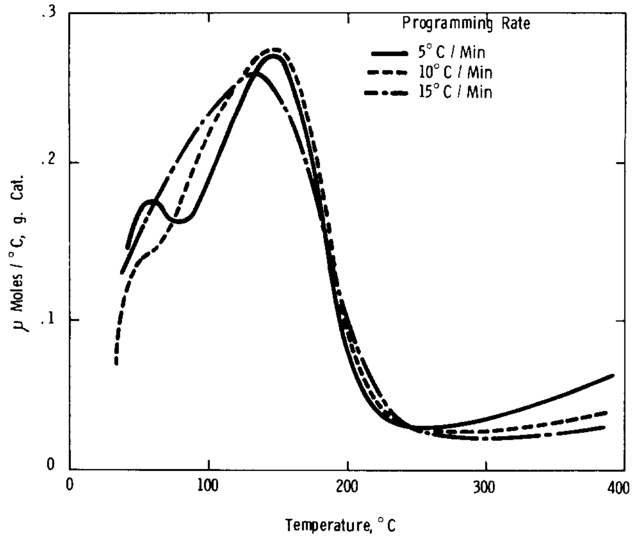

FIG. 4. Desorption spectra for 0.6 wt% Ir/γ-Al_2O_3 at programming rates of 5, 10, and 15°C/min.

Analysis of Desorption Spectra

i. Stoichiometry. The desorption spectra for Ir/γ-Al_2O_3 at various metal loadings are shown in Fig. 5. At a loading of 0.2 wt% a primary peak is seen at 153°C along with a rider peak at 43°C. The primary peak is bell shaped in contrast to sharp peaks observed at higher metal loadings. The desorption spectrum for 0.4 wt% Ir shows a primary peak at 157°C along with a rider peak at 43°C. The rider peak shifts to 61°C at a metal loading of 0.6 wt% Ir. The primary peak for this sample was observed at 145°C. The primary and rider peaks are not well resolved at an iridium loading of 1 wt% Ir. Only a single peak is observed at 141°C. The area under each peak in micromoles hydrogen/micromole iridium at each metal loading is given in Table 1.

A comparison of the desorption spectra in the range of metal loadings from 0.2 to

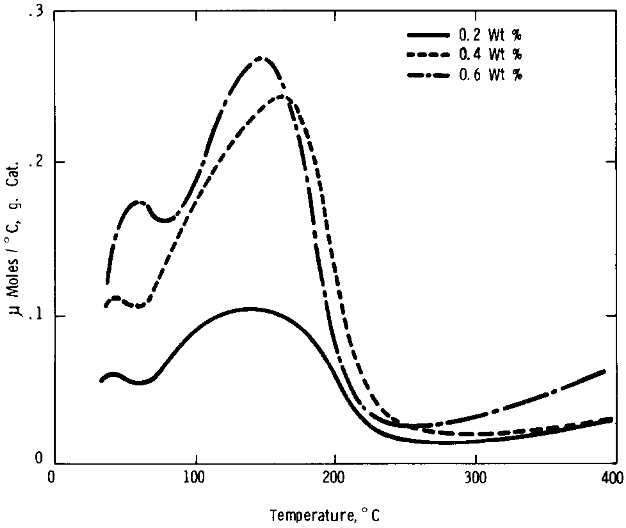

FIG. 5. Desorption spectra for Ir/γ-Al_2O_3.

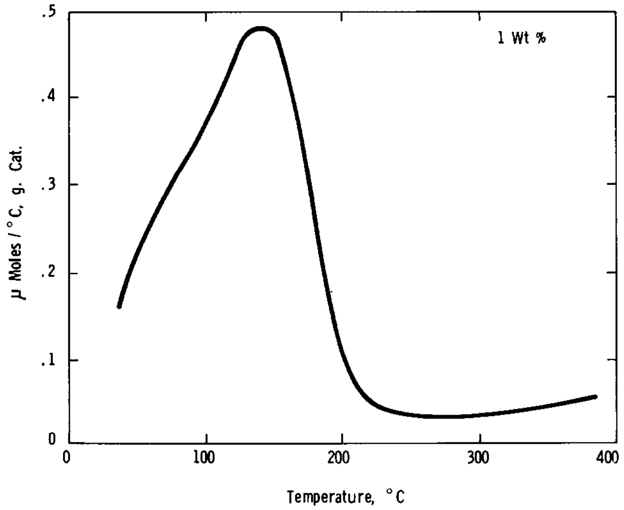

FIG. 6. Desorption spectrum for 1.0 wt% Ir/γ-Al_2O_3.

1.0 wt% indicates a primary peak around 150°C and a rider peak between 40 and 60°C. The commencement of a third peak around 300°C is also observable in Fig. 5. This is attributed to desorption of spillover hydrogen from the alumina support. Kramers and Andre (*12*) have also observed the desorption of atomic hydrogen from alumina to occur with a peak at 480°C. This peak is not readily observable in Fig. 6 due to the high desorption rates of hydrogen from the iridium.

The ratio of atomic hydrogen under the second peak to iridium is seen from Table 1 to be approximately two at all metal loadings. In a recent study on Ir/η-Al_2O_3, McVicker *et al.* (*6*) found that a certain fraction of chemisorbed hydrogen could be reversibly desorbed at room temperature. They also found the dispersion based on the irreversibly bound hydrogen to be two hydrogen atoms per iridium atom. In the present case we believe that the area under the first peak represents loosely held (physisorbed) hydrogen and the area under the second peak the strongly held fraction. Evi-

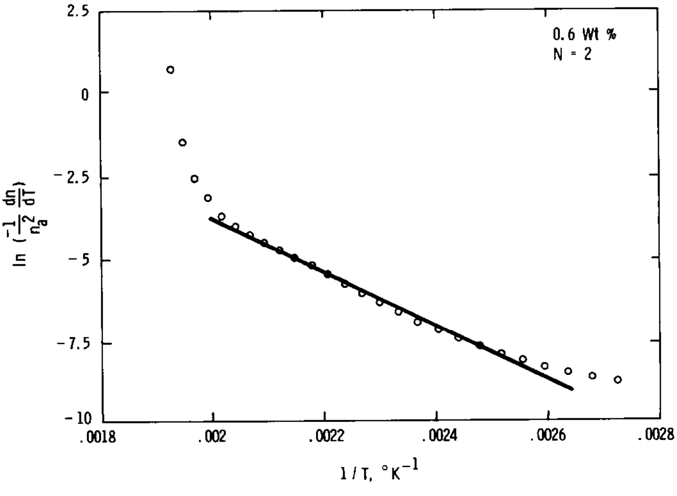

FIG. 7. Arrhenius plot for 0.6 wt% Ir/γ-Al_2O_3.

TABLE 2

CO Chemisorption on Ir/γ-Al_2O_3

Number	Metal loading, wt%	CO Adsorbed µmol/g cat	CO/Ir molar ratio
1	0.26	29.58	2.2
2	0.48	45.12	1.81
3	0.56	56.3	1.86
4	0.95	71.24	1.44

dence to support this argument comes from accompanying CO adsorption isotherms performed on the same samples. The results (Table 2) indicate that approximately two CO molecules are adsorbed per iridium atom at all metal loadings.

Due to the nature of the desorption spectrum for the 1 wt% Ir sample, it was not possible to calculate the area under each peak individually. However, the strongly held fraction could be estimated in the following manner. As will be shown in the next section, the desorption of hydrogen from iridium was found to follow second-order kinetics. Under these circumstances the desorption spectrum is expected to be symmetric about the temperature T_{max} at which the rate of desorption is a maximum (*13*). It was, therefore, possible to calculate the area under the desorption spectrum between T_{max} and the end of the profile and estimate the strongly held fraction by doubling the area. Results obtained in this manner were found to be in good agreement with the values calculated from the CO adsorption experiments (Table 2).

TABLE 3

Activation Energy for Desorption of Hydrogen from Ir/γ-Al_2O_3

Number	Ir loading wt%	E_d kcal/mol	
1	0.26	12.24[a]	11.56[b]
2		13.16	13.32
3	0.48	15.54	17.43
4		17.72	15.48
5	0.56	16.60	17.69
6		15.03	16.09
7		17.91	15.65
8		16.28	14.89
9	0.95	16.18	15.49
10		15.27	16.21
11		18.24	15.77

[a] Calculated from Arrhenius analysis.

[b] Calculated from Eq. (7).

ii. Order and activation energy of desorption. Using Eq. (4) and data from the TPD profiles at iridium loadings of 0.2–1.0 wt%, straight lines were obtained for $N = 2$ in the temperature range of 85–200°C. A sample plot is shown in Fig. 7 for an iridium loading of 0.6 wt%. This indicates that hydrogen is dissociatively adsorbed on iridium in the following manner.

$$Ir + H_2 \rightarrow H\text{-}Ir\text{-}H$$

The activation energies calculated from the slopes of the straight lines are provided in Table 3.

In the present case the activation energy can also be calculated as follows. For a second-order desorption it can be shown that the TPD profile is symmetric about T_{max} and consequently

$$n_a|_{max} = n_a/2|_{total}.$$

Substituting for N and $n_a|_{max}$ in Eq. (6), we get

$$E_d = \frac{4(dn_a/dT)_{max}}{n_a|_{total}} RT^2\Big|_{max}. \tag{7}$$

Thus knowing the maximum desorption rate $(dn_a/dT)_{max}$, the temperature T_{max} at which the desorption rate goes through a maximum, and the total amount of desorbed gas, the activation energy can be calculated.

The activation energies calculated from the Arrhenius analysis compare favorably with those calculated from Eq. (7), as shown in Table 3. A sample calculation is provided in Appendix 1.

In summary, the stoichiometry of hydrogen and CO chemisorption on Ir/γ-Al_2O_3 at metal loadings of 0.2–1.0 wt% was found to be H/Ir = CO/Ir = 2. The desorption spectra of hydrogen from Ir/γ-Al_2O_3 show a primary peak around 150°C and a rider peak between 40 and 60°C. The hydrogen under the primary peak is believed to be bound strongly to the iridium and that under the rider peak to be loosely held (physisorbed). A mathematical analysis of the desorption spectra indicates that the chemisorption of hydrogen occurs dissociatively on iridium. The activation energy of desorption was found to be in the range of 11–17 kcal/g mol.

APPENDIX 1

Sample calculations for the activation energy using Eq. (6) and data from Run 8 (Table 1). From the desorption spectrum

$$\left(\frac{dn_a}{dT}\right)\bigg|_{\max} = 0.27169\ \mu\text{mol/g cat, °K}$$

$$T_{\max} = 145.04°\text{C}$$

$$n_a\bigg|_{\text{total}} = \int_0^\infty \left(\frac{dn_a}{dT}\right) dT.$$

Since a second-order profile is symmetric about $T = T_{\max}$ (*13*)

$$n_a\bigg|_{\text{total}} = 2\int_{T_{\max}}^\infty \left(\frac{dn_a}{dT}\right) dT = 25.32\ \mu\text{mol/g cat.}$$

Therefore

$$E_d = \frac{4 \times 0.27167}{25.32} \times 1.987 \times (145.04 + 273.16)^2 = 14.89\ \text{kcal/g mol.}$$

APPENDIX 2: NOMENCLATURE

n_a	Concentration of adspecies, μmol/g cat
t	Time, min
N	Order of desorption
k_{do}	Pre-exponential factor
E_d	Activation energy for desorption, cal/g mol
R	Gas constant, cal/g mol, K
T	Temperature, K

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