JOURNAL OF CATALYSIS 79, 251–258 (1983)

H_2–D_2 Equilibration over Supported Iridium Catalysts Prepared from $Ir_4(CO)_{12}$

KATSUMI TANAKA, KENNETH L. WATTERS, AND RUSSELL F. HOWE[1]

Laboratory for Surface Studies and Department of Chemistry, University of Wisconsin, Milwaukee Wisconsin 53201

AND

S. LARS T. ANDERSSON

Department of Chemical Technology, Lund Institute of Technology, Chemical Center, Lund, Sweden

Received March 8, 1982; revised September 21, 1982

X-Ray photoelectron spectroscopy (XPS) measurements have been performed on silica- and alumina-supported iridium catalysts prepared from $Ir_4(CO)_{12}$, and the activity of these catalysts for the $H_2 : D_2$ equilibration reaction determined as a function of the activation treatment. The XPS results show that predominantly zerovalent iridium is obtained upon decomposition of supported $Ir_4(CO)_{12}$ *in vacuo*. Maximum activity for $H_2 : D_2$ equilibration is generated only after removal of all carbonyl ligands. The reaction is poisoned by readsorption of CO, and the recovery of activity upon desorption of CO parallels the original generation of activity.

INTRODUCTION

The preparation of heterogeneous catalysts from transition metal cluster carbonyl complexes is receiving widespread attention. The comprehensive review by Bailey and Langer (*1*) provides a recent summary of the literature in this area. The thermal decomposition of cluster carbonyl complexes adsorbed on high-surface-area oxide supports is invariably accompanied by rearrangement of the metal clusters, sintering, and/or reaction with the support. Thus the original goal (*2*) of preparing supported metal atom clusters of well-defined geometry by decomposition of complexes with known structure has not in general been achieved. Nevertheless, supported metal catalysts prepared from cluster complexes show high metallic dispersions and in some cases novel catalytic properties. Considerable interest thus remains in characterizing such materials and in investigating the manner in which active sites are generated.

The preparation of silica- and alumina-supported iridium catalysts from the cluster complex $Ir_4(CO)_{12}$ was first reported by Anderson *et al.* (*3*, *4*) and Howe (*5*). Subsequently, the activity of such catalysts has been investigated for alkane hydrogenolysis (*6*) and carbon monoxide hydrogenation (*7*). In the catalytic studies to date, however, the catalyst pretreatments have included high-temperature reduction in hydrogen following decomposition of the $Ir_4(CO)_{12}$. No information was thus obtained concerning the generation of catalytically active species during decomposition of the adsorbed $Ir_4(CO)_{12}$.

We have recently described the detailed characterization of silica- and alumina-supported iridium catalysts prepared from $Ir_4(CO)_{12}$ by means of infrared spectroscopy, temperature-programmed desorption, and gravimetric chemisorption measurements (*8*). The present paper extends that study in two ways: X-ray photoelec-

---

[1] Address correspondence to this author at the Chemistry Department, University of Auckland, Private Bag, Auckland, New Zealand.

0021-9517/83/020251-08$03.00/0

tron spectroscopy (XPS) has been used to determine iridium binding energies in the various catalysts, and the catalytic activity for the $H_2:D_2$ equilibration reaction has been measured as a function of the catalyst activation treatment. The equilibration reaction is known to proceed rapidly over the Group 8 metals, and is considered to be structure insensitive, or *facile,* under the usual conditions (*9*). The generation of activity for $H_2:D_2$ equilibration upon decomposition of adsorbed $Ir_4(CO)_{12}$ may thus be used to follow the generation of metallic iridium sites.

EXPERIMENTAL

The preparation of the silica- and alumina-supported $Ir_4(CO)_{12}$ catalysts used in this work has been described in detail elsewhere (*8*). For the XPS experiments a silica-supported catalyst containing 1.05 wt% iridium (determined by analysis after decomposition of the adsorbed $Ir_4(CO)_{12}$) and an alumina-supported catalyst containing 3 wt% iridium were employed. For the $H_2:D_2$ equilibration experiments, the same silica-supported catalyst and an alumina-supported catalyst containing 1.34 wt% iridium were used. A conventional silica-supported iridium catalyst (0.94 wt%) was prepared following Anderson and Foger (*6*) by impregnation of the support with aqueous $(NH_4)_2IrCl_6$, followed by calcination in air at 500°C and reduction in hydrogen at 350°C. The gases used in the catalytic experiments were purified by passage over liquid nitrogen-cooled charcoal and molecular sieve traps. The D_2 contained 3% HD.

XPS measurements were performed on catalyst samples pressed onto gold foil or silver mesh with an AEI ES200B spectrometer (*10*), using Al$K\alpha$ radiation. Sample charging effects were corrected for by referencing all binding energies to the 84.0-eV line of gold, which was vacuum-deposited onto selected samples. Binding energies quoted are considered accurate to ±0.2 eV. Unless otherwise stated, all sample treatments were carried out *in situ*. With the alumina-supported catalyst, the iridium $4f$ lines were partially obscured by an Al $2p$ line at 64.6 eV from the support (excited by the Al$K\alpha_{3,4}$ satellite of the Al$K\alpha$ radiation); subtraction of the support line from the observed spectra was performed on a Tetronix 4051 linked to a 4662 interactive digital plotter. The binding energies in the subtracted spectra are considered accurate to ±0.4 eV.

$H_2:D_2$ equilibration measurements were conducted in an all-glass recirculation reactor of total volume 350 ml. A constant catalyst loading of 0.100 g and a total pressure of 100 Torr (initially $H_2:D_2 = 1:1$) were used. Samples of the gas phase were removed at known time intervals and their composition determined with a Hitachi RMU-6E mass spectrometer (70-V ionization). The sensitivity of the instrument for H_2, D_2, and HD was calibrated with known mixtures. First-order rate constants for the equilibration reaction were determined by plotting the equation

$$\ln\left\{\frac{[HD]_e - [HD]_0}{[HD]_e - [HD]_t}\right\} = k_1 t,$$

where $[HD]_e$ is the mole fraction of HD at equilibrium, $[HD]_0$ the initial mole fraction, and $[HD]_t$ the mole fraction at time t. All of the data obtained fitted the first-order equation. The first-order rate constants were normalized to the amount of iridium in the catalysts, and the reaction rate calculated in the usual way from the rate constant and the total number of molecules present.

The rate of the equilibration reaction was measured between 77 K and room temperature following successive stepwise activation of the silica- and alumina-supported $Ir_4(CO)_{12}$ catalysts *in vacuo* between 100 and 350°C at 50°C intervals (1 h at each temperature). The catalysts were then reduced in H_2 at 350°C and the equilibration rate measured again. Carbon monoxide poisoning experiments were carried out by exposing the reduced catalysts to excess CO (20 Torr at room temperature), then measuring the equilibration rate following subsequent stepwise desorption of CO between room temperature and 350°C, and further reduction. The activity of the conventional silica-supported iridium catalyst was measured following hydrogen reduction at 350°C.

RESULTS

XPS Measurements

Figure 1 shows X-ray photoelectron spectra of a series of iridium samples in the binding energy range 55–70 eV (where the Ir $4f_{7/2}$ and $4f_{5/2}$ core lines appear). The Ir $4f_{7/2}$ binding energies of the samples illustrated in the figure and of a range of other iridium-containing materials are listed in Table 1.

TABLE 1

Iridium $4f_{7/2}$ Binding Energies for Some Iridium Catalysts

Sample	Ir $4f_{7/2}$ (±0.2 eV)
This work[a]	
$Ir_4(CO)_{12}$ (s)	62.8
Ir foil	60.8
$Ir_4(CO)_{12}$ on SiO_2	62.3
Decomposed *in vacuo*, 400°C	61.5
Reduced in H_2, 310°C	61.5
Conventional Ir-SiO_2, oxidized	62.8
Reduced in H_2, 400°C	61.6
$Ir_4(CO)_{12}$ on Al_2O_3	61.9[b]
Decomposed *in vacuo*, 380°C	61.4[b]
$(Ir(III)(NH_3)_5Cl)Cl_2$ (s)	62.5
$(NH_4)_2Ir(IV)Cl_6$ (s)	64.0
Ir(III) X zeolite[c]	62.7[b]
Ref. (*19*)	
Ir foil	60.75
Refs. (*14, 20, 21*)[d]	
Ir metal	60.1–60.5
Conventional Ir–SiO_2, reduced	61.0
Conventional Ir–α-Al_2O_3	61.1
Conventional Ir–η-Al_2O_3	61.3–61.6
Conventional Ir–δ-Al_2O_3	61.9

[a] Referenced to Au $4f_{7/2}$ = 84.0 eV.

[b] Obtained by subtraction, ±0.4 eV.

[c] Prepared by ion exchange of $Ir(NH_3)_5Cl^{2+}$ into NaX, evacuated at 300°C.

[d] Referenced to C 1*s* = 284.0 or 284.4 eV.

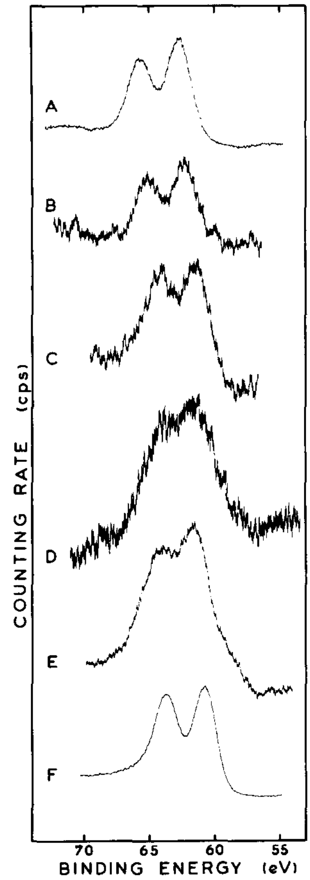

FIG. 1. X-Ray photoelectron spectra of iridium samples. (A) Solid $Ir_4(CO)_{12}$; (B) $Ir_4(CO)_{12}$–SiO_2 catalyst, as prepared; (C) activated *in vacuo* at 400°C; (D) reduced in H_2 at 310; (E) conventional Ir–SiO_2 catalyst, reduced in H_2 at 400°C; (F) Ir foil.

The $4f_{7/2}$ binding energy for solid $Ir_4(CO)_{12}$ (Fig. 1A) is 2.0 eV higher than that of iridium metal (Fig. 1F). The silica-supported $Ir_4(CO)_{12}$ catalyst as prepared showed a slight shift to lower binding energy relative to solid $Ir_4(CO)_{12}$ (Fig. 1B), but activation of the catalyst *in vacuo* up to 400°C caused a much larger shift (Fig. 1C). Subsequent reduction in H_2 at 310°C for 12 h caused some broadening of the doublet, but no further change in binding energy (Fig. 1D). The conventional silica-supported iridium catalyst which had been reduced in flowing H_2 at 400°C gave an Ir $4f$ spectrum identical to that of the reduced catalyst derived from $Ir_4(CO)_{12}$ (Fig. 1E).

The Ir $4f$ doublet could be clearly resolved in the case of the alumina-supported $Ir_4(CO)_{12}$ catalyst only after subtraction of the Al $2p$ line from the support, which introduced a larger uncertainty in the absolute binding energies (±0.4 eV). The Ir $4f_{7/2}$ binding energy of the alumina-supported $Ir_4(CO)_{12}$ catalyst following decomposition *in vacuo* at 380°C was close, however, to that of the corresponding silica-supported catalyst (Table 1). Also listed in Table 1 are binding energies measured for two reference compounds, $Ir(NH_3)_5Cl_3$ and $(NH_4)_2IrCl_6$, in which the formal oxidation state of the iridium is 3+ and 4+, respectively.

$H_2 : D_2$ *Equilibration*

Figure 2a shows the rate of the equilibration reaction at 77 K over the alumina-supported $Ir_4(CO)_{12}$ catalyst as a function of the temperature of activation of the catalyst, and of the temperature of desorption of CO subsequently adsorbed. The reaction rate determined in blank experiments with the alumina support alone (pretreated under identical conditions) was subtracted in each case (this amounted to less than 0.5% of the maximum rate obtained from the iridium catalysts).

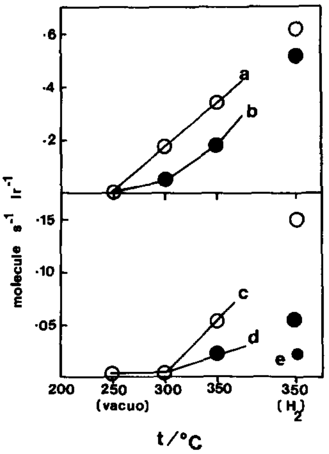

FIG. 2. Specific rate of $H_2 : D_2$ equilibration at 77 K as a function of catalyst pretreatment. (a) $Ir_4(CO)_{12}$–Al_2O_3, initial activation; (b) following CO poisoning; (c) $Ir_4(CO)_{12}$–SiO_2, initial activation; (d) following CO poisoning; (e) conventional Ir–SiO_2 catalyst.

Significant activity for $H_2 : D_2$ equilibration was generated only after activation of alumina-supported $Ir_4(CO)_{12}$ *in vacuo* above 250°C. The reaction rate at 77 K increased linearly with activation temperature between 250 and 350°C, and a further two-fold increase occurred upon subsequent reduction in H_2 at 350°C. The apparent activation energy for the reaction was estimated from measurements of the rate between 77 K and room temperature to lie between 1 and 2 kcal mol^{-1}.

Adsorption of CO at room temperature on the reduced iridium–alumina catalyst completely poisoned the equilibration reaction (the CO uptake on this catalyst was previously measured to be 1.32 CO per iridium (*8*)). On subsequent desorption of CO by heating *in vacuo*, significant activity was regenerated only above 250°C, and after reduction in H_2 at 350°C activity close to that of the unpoisoned catalyst was obtained (Fig. 2b).

Similar experiments were conducted with silica-supported $Ir_4(CO)_{12}$. Figure 2c shows the reaction rate at 77 K as a function of the initial activation temperature and the temperature of desorption of CO subsequently adsorbed. For this catalyst, activation *in vacuo* above 300°C was required to generate significant equilibration activity, and reduction in H_2 at 350°C caused a further three-fold increase in activity. CO adsorption completely poisoned the catalyst (1.34 CO per iridium), and evacuation above 300°C was necessary to regenerate significant activity. The original activity of the unpoisoned catalyst could not be completely restored however, even by further reduction in H_2 at 350°C (Fig. 2d). Also shown in Fig. 2e is the reaction rate for a conventional silica-supported iridium catalyst which had been reduced in H_2 at 350°C. The kinetic parameters measured for the various catalysts are summarized in Table 2.

TABLE 2

$H_2 : D_2$ Equilibration Kinetic Data

Catalyst[a]		k_1 at 77 K[b] (s^{-1})	Specific reaction rate (molecule s^{-1} Ir^{-1})	E_a (kcal mol^{-1})
Al_2O_3 support	(350)	9.2×10^{-6}	—	—
SiO_2 support	(350)	7.5×10^{-6}	—	—
$Ir_4(CO)_{12}$–Al_2O_3	(50)	1.5×10^{-5}	—	—
	(200)	1.7×10^{-5}	—	1.8
	(250)	1.7×10^{-5}	0.0018	1.8
	(300)	8.1×10^{-4}	0.18	1.8
	(350)	1.5×10^{-3}	0.34	—
H_2 reduced	(350)	2.7×10^{-3}	0.62	—
$Ir_4(CO)_{12}$–SiO_2	(50)	5.8×10^{-6}	—	—
	(200)	1.1×10^{-5}	—	—
	(250)	2.1×10^{-5}	0.0035	—
	(300)	2.4×10^{-5}	0.0043	—
	(350)	1.8×10^{-4}	0.052	—
H_2 reduced	(350)	5.2×10^{-4}	0.15	—
Ir–SiO_2, reduced		9.6×10^{-5}	0.026	—
Pt, Ref. (*11*)		—	0.04	2.2
Pt, Ref. (*11*)		—	0.23	0
Pt, Ref. (*9*)		—	0.0008[c]	2.5
Pd, Ref. (*9*)		—	0.004[c]	2.1

[a] Activation temperature is in parentheses.

[b] Experimental first-order rate constant.

[c] Extrapolated from room temperature.

DISCUSSION

XPS Measurements

The infrared and temperature-programmed desorption (TPD) measurements described earlier (*8*) showed that $Ir_4(CO)_{12}$ supported on silica and alumina decomposes on heating *in vacuo* above 100°C, and that decomposition is almost complete at 300°C. From infrared and gravimetric CO absorption measurements it was concluded that the product of decomposition of $Ir_4(CO)_{12}$ on silica was zerovalent iridium, whereas on alumina a mixture of zerovalent and oxidized iridium species was formed. Additional evidence for oxidation of $Ir_4(CO)_{12}$ on alumina during decomposition has been presented by Hucul and Brenner (*12*). The decomposition of $Ir_4(CO)_{12}$ on both silica and alumina was irreversible, and reduction in H_2 at 350°C gave metal dispersions comparable with the most highly dispersed conventional supported iridium catalysts, as measured by CO adsorption capacity.

The XPS results for silica-supported $Ir_4(CO)_{12}$ are completely consistent with the conclusions reached earlier (*8*). The Ir $4f_{7/2}$ binding energy of the catalyst as prepared is marginally lower than that of bulk $Ir_4(CO)_{12}$, consistent with the notion that the freshly prepared catalyst consists of small crystallites of $Ir_4(CO)_{12}$ dispersed through the support (*4*, *8*). Of greater significance is the 2.0-eV difference between $Ir_4(CO)_{12}$ and iridium metal. Similar differences between cluster carbonyl complexes and the bulk metal have been seen for

$Rh_6(CO)_{16}$ (*10*) and $[Pt_3(CO)_6]_n^{2-}$ (*13*), and have been attributed to a combination of electron transfer from the metal to carbonyl ligands and a diminished extraatomic relaxation relative to the bulk metal (*13*). In the case of $Ir_4(CO)_{12}$, the binding energy of the formally zerovalent Ir is close to that of Ir(III).

Decomposition of silica-supported $Ir_4(CO)_{12}$ *in vacuo* at 400°C lowers the Ir binding energy by 0.8 eV, and subsequent reduction caused no further shift. The resulting binding energies are identical within experimental uncertainty to that of the conventional silica-supported catalyst. These values are, however, significantly higher than that of bulk iridium, a difference which warrants further comment. Several XPS studies of conventional supported iridium catalysts have been reported by Contour and co-workers (*14, 20, 21*). The absolute binding energies given by these authors cannot be compared exactly with those obtained here, since their data were referenced to the impurity C 1*s* line (taken as 284 eV (*14*) or 284.4 eV (*20, 21*)), rather than the Au $4f_{7/2}$ line. However, all of the iridium catalysts examined by Contour and co-workers showed a shift of the Ir 4*f* doublet to higher binding energy relative to the bulk metal. For example, their 0.5 to 0.9-eV difference between bulk and silica-supported iridium compares favorably with the 0.7-eV shift found here. The increase in binding energy was attributed to a metal–support interaction involving partial electron transfer from the metal to the support. The magnitude of the shift was shown to correlate with the acidity of the support (*14, 20, 21*).

In the case of alumina-supported $Ir_4(CO)_{12}$, the catalyst as prepared shows a binding energy almost 1 eV lower than that of the bulk complex. Infrared spectra (*4, 5, 8*) indicate that the complex is molecularly adsorbed from solution onto the alumina surface during catalyst preparation; thus the XPS result suggests that the adsorbed complex has a binding energy significantly different from that of the bulk (keeping in mind the relatively large uncertainty due to subtraction of the support spectrum). Decomposition of $Ir_4(CO)_{12}$ on alumina *in vacuo* causes a further reduction in binding energy, to a value close to that of the reduced silica-supported catalysts. Binding energy differences between conventional silica- and alumina-supported catalysts of up to 0.9 eV have been reported (*14, 20, 21*). These differences may, however, merely reflect variations in the difficulty of fully reducing the conventional alumina-supported iridium. The x-ray photoelectron spectra show no evidence of oxidation of iridium during decomposition of $Ir_4(CO)_{12}$ adsorbed on alumina, but it must be pointed out that the iridium loading of the alumina-supported catalyst used in the XPS experiments was considerably higher than that used in the infrared (*8*) and TPD (*12*) measurements (in order to obtain satisfactory signal-to-noise ratios). Mild oxidation of a fraction of the iridium present may have escaped detection by XPS.

$H_2:D_2$ *Equilibration*

The $H_2:D_2$ equilibration reaction has been previously studied on many different metal catalysts. Of the Group 8 metals, platinum has received the most attention. Ross and Stonehart (*9*) concluded that under the conditions used by them (Pt wire catalysts, total pressure 0.2–10 Torr, 273–473 K) equilibration proceeded via a dissociative (Bonhoeffer–Farkas) mechanism, and that the dissociation was structure insensitive in the classification of Boudart *et al.* (*15*). This agreed with earlier observations (*16*) that the equilibration rate over alumina-supported platinum catalysts was independent of particle size. In contrast, Somorjai and co-workers (*17*) found in molecular-beam experiments that step sites on single-crystal platinum surfaces were more active for $H_2:D_2$ equilibration than terrace sites. However, as pointed out by Ross and Stonehart (*9*), the beam experiments were conducted under conditions of high temperature and low hydrogen surface coverage, where hydrogen desorption (which is favored on low-energy surface sites) determines the reaction rate. Under conditions of high surface coverage, the reaction becomes structure insensitive.

There appear to be no detailed kinetic data in the literature for $H_2:D_2$ equilibration over supported iridium catalysts. No attempt has been made in the present work to investigate the reaction mechanism. At 77 K a Rideal–Eley mechanism involving attack of molecular hydrogen on adsorbed atoms may be more likely than the completely dissociative Bonhoeffer–Farkas mechanism (as has been suggested for platinum (*11, 18*)). Regardless of the exact mechanism of equilibration over supported iridium (and it should be noted that the apparent activation energies measured here are close to those reported for platinum and palladium), it seems likely that under the conditions used in the present work the reaction is structure insensitive. The reaction rate is therefore determined by the number of active sites available.

Although it is not possible to make quantitative comparisons of the published TPD curves (*8, 12*) with the curves in Fig. 2 showing generation of activity as a function of activation temperature, it appears that significant equilibration activity is generated only after desorption of CO is almost complete. The further increase in activity upon hydrogen reduction of the alumina-supported catalyst may be attributed to an increase in the number of metallic sites due to reduction of that fraction of the iridium which was oxidized during decomposition of $Ir_4(CO)_{12}$ *in vacuo* (the twofold increase in activity should be compared with an increase in CO adsorption capacity from 0.69 to 1.32 CO per iridium upon reduction (*8*)). Reduction of the silica-supported catalyst, however, caused a comparable increase in activity, although the CO adsorption capacity of this catalyst was determined to increase only from 1.21 to 1.34 CO per iridium upon reduction (*8*), and the XPS experiments revealed no evidence for oxidation of iridium during decomposition of $Ir_4(CO)_{12}$ on SiO_2. A possible explanation would be that chemisorption of H_2 is inhibited to a greater extent than that of CO by traces of carbon formed in the disproportionation of carbonyl ligands during activation *in vacuo*. (Evidence for the disproportionation reaction comes from the detection of CO_2 desorption during activation *in vacuo* above 300°C (*8*).)

The complete poisoning of the equilibration reaction upon adsorption of a monolayer of CO is consistent with the observations of Ross and Stonehart (*9*) on platinum and rhodium catalysts. These authors found that the equilibration rate was proportional to $(1-\theta_{CO})^2$, which implies that two adjacent metal atom sites are required for the equilibration reaction. A similar nonlinear dependence of reaction rate on CO coverage is observed here. Appreciable activity is regenerated for both the silica- and alumina-supported iridium catalysts only after more than 75% of the adsorbed CO has been removed, as estimated from the TPD curves (*8*). The original activity of the unpoisoned catalysts could not be completely regenerated by desorption of CO *in vacuo* up to 350°C. The desorption of CO is accompanied by significant quantities of CO_2, attributed to the disproportionation reaction (*8*). As with freshly activated catalysts, the carbon produced may poison the exchange reaction. Subsequent treatment with H_2 at 350°C increased the activity of both catalysts.

The similarity of the curves (Fig. 2) for generation of activity in fresh catalysts and regeneration of activity in CO-poisoned catalysts suggests that the original activity is generated upon desorption of CO from metallic iridium sites rather than as a result of some modification or rearrangement of the iridium clusters during activation above 250°C. If, as suggested above, the active sites for the equilibration reaction consist of two or more adjacent metal atoms, then high concentrations of such sites are generated only upon removal of the last traces of CO.

The absolute values of the specific rates at 77 K for various catalysts may be usefully compared (Table 2). The dispersions of the alumina- and silica-supported iridium catalysts prepared from $Ir_4(CO)_{12}$ are almost identical; the fourfold difference in specific rate between these catalysts following H_2 reduction at 350°C thus reflects a difference in the intrinsic activity of the iridium sites, possibly due to support interactions. The dispersion of the conventional silica-supported catalyst was not measured, but the preparation conditions were closely similar to those used by Anderson and Foger (*6*), who reported a dispersion of 0.16 for this catalyst. The lower specific rate for the conventional silica-supported catalyst may thus be entirely due to its lower dispersion. The magnitudes of all specific rates measured here for iridium catalysts compare favorably with those reported for platinum and palladium. The activities of the iridium catalysts are several orders of magnitude higher than those of transition metal oxides such as Cr_2O_3 or Co_3O_4 at 77 K (*22*). The enhancement of activity upon reduction and the strong poisoning effect of CO indicate that oxidized iridium species do not play a significant role in the catalysis of H_2–D_2 equilibration.

ACKNOWLEDGMENTS

This work was supported by Grant CHE 77-20373 from the National Science Foundation. S.L.T.A. thanks Professor S. Lundin for his support.

REFERENCES

1. Bailey, D. C., and Langer, S. H., *Chem. Rev.* **81,** 110 (1981).

2. Anderson, J. R., "Structure of Metallic Catalysts," p. 275. Academic Press, New York, 1975.

3. Anderson, J. R., and Howe, R. F., *Nature (London)* **268,** 129 (1977).

4. Anderson, J. R., Elmes, P. S., Howe, R. F., and Mainwaring, D., *J. Catal.* **50,** 508 (1977).

5. Howe, R. F., *J. Catal.* **50,** 196 (1977).

6. Anderson, J. R., and Foger, K., *J. Catal.* **59,** 325 (1979).

7. Ichikawa, M., and Shikakura, K. *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," paper B17.

8. Tanaka, K., Watters, K. L., and Howe, R. F., *J. Catal.* **75,** 23 (1982).

9. Ross, P. N., and Stonehart, P., *J. Catal.* **35,** 391 (1974).

10. Andersson, S. L. T., Watters, K. L., and Howe, R. F., *J. Catal.* **69,** 212 (1981).

11. Breakspere, R. J., Eley, D. D., and Norton, P. R., *J. Catal.* **27,** 215 (1972).

12. Hucul, D. A., and Brenner, A., *J. Amer. Chem. Soc.* **103,** 217 (1981).

13. Apai, G., Lee, S. T., Mason, M. G., Gerenser, L. J., and Gardner, S. A., *J. Amer. Chem. Soc.* **101,** 6880 (1979).

14. Escard, J., Pontvianne, B., and Contour, J. P., *J. Electron Spectrosc.* **6,** 17 (1975).

15. Boudart, M., Aldag, A., Benson, J. E., Dougherty, N. A., and Harkins, C. G., *J. Catal.* **6,** 92 (1966).

16. Poltorak, O. M., and Boronin, V. S., *Russ. J. Phys. Chem.* **40,** 1436 (1966).

17. Salmeron, M., Gale, R. J., and Somorjai, G. A., *J. Chem. Phys.* **67,** 5324 (1977).

18. Tsuchiya, S., Amenomiya, Y., and Cvetanovic, R. J., *J. Catal.* **20,** 1 (1971).

19. Nyholm, R., Berndtsson, A., and Martensson, N., *J. Phys. C* **13,** L1091 (1980).

20. Escard, J., Leclère, C., and Contour, J. P., *C.R. Acad. Sci. Ser. C* **274,** 1645 (1972).

21. Leclère, C., Contour, J. P., and Pannetier, G., *Ann. Chim.* **9,** 221 (1974).

22. Dowden, D. A., Mackenzie, N., and Trapnell, B. W., *Proc. R. Soc. London Ser. A* **237,** 245 (1956).