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Preparation of Some Supported Metallic Catalysts from Metallic Cluster Carbonyls

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An examination was made of the adsorption of some metallic cluster carbonyls (MCCs), $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $Ru_3(CO)_{12}$, from nonaqueous solution onto two typical catalyst supports, γ-alumina and Aerosil silica. With two MCCs, $Co_2Rh_2(CO)_{12}$ and $Ir_4(CO)_{12}$, dispersed metallic catalysts were generated, and a study was made of how the main experimental conditions affected the metallic dispersion. MCC adsorption was more facile on γ-alumina than on silica and was often assisted by the presence of oxygen. An ir study showed that initial adsorption of $Co_2Rh_2(CO)_{12}$ on γ-alumina occurred with the loss of bridging carbonyls, the remaining carbonyls being progressively lost at temperatures >300 K, while adsorption of $Ir_4(CO)_{12}$ on γ-alumina resulted in progressive carbonyl loss at 320–620 K. Strong adsorption involves carbonyl loss, probably by ligand exchange with a surface anion, and the effect of oxygen is probably oxidative decarbonylation. Catalysts prepared from $Co_2Rh_2(CO)_{12}$ or $Ir_4(CO)_{12}$ were relatively highly dispersed ($D \approx 0.4$–1 depending on conditions), and $Co_2Rh_2(CO)_{12}$ gave a much higher dispersion than was obtained by conventional impregnation using aqueous salt solutions. MCC adsorption in the presence of oxygen favored higher dispersions.

The use of transition metal carbonyls for the preparation of dispersed metallic catalysts was suggested by Parkyns (*1*) who showed that $Ni(CO)_4$ decomposed on an alumina surface to give metallic nickel. However, the use of metallic cluster carbonyls (MCCs) for this purpose was suggested independently and much more recently by Anderson and Mainwaring (*2*), Robertson and Webb (*3*), and Smith *et al.* (*4*). The present paper is intended to give a more detailed account of this method.

Following the general principles which control the nature of supported metallic catalysts prepared by impregnation or adsorption methods (*5*), we have examined the adsorption of some MCCs, ($Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $Ru_3(CO)_{12}$), from solution onto two typical supports (γ-alumina and silica), and with two of these ($Co_2Rh_2(CO)_{12}$ and $Ir_4(CO)_{12}$) we have examined how the main experimental conditions affect the resultant catalyst dispersion.

MATERIALS AND APPARATUS

Supports

Silica: Aerosil, Degussa 200 (200 m^2 g^{-1}); γ-alumina: Harshaw 1401 P (200 m^2 g^{-1}) and Wohlm γ-alumina (200 m^2 g^{-1}).

Metallic Cluster Carbonyls

The $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $Ru_3(CO)_{12}$ were used as obtained from Strem

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TABLE 1

Adsorption of Various Metallic Cluster Carbonyls from Nonaqueous Solution

Support	MCC	MCC solution	Support pretreatment	Adsorption conditions	Extent of MCC adsorption (%)	Comments
γ-Al_2O_3	$Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, or $Co_4(CO)_{12}$	4 mg cm^{-3} in *n*-hexane	Various temperatures, 400–630 K; 16 h *in vacuo*	0.5 g of support + 5 cm^3 of MCC solution, anhydrous, oxygen-free; 5 min, 293 K	100	No MCC recovered by washing with *n*-hexane at 293 K
SiO_2	$Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, or $Co_4(CO)_{12}$	4 mg cm^{-3} in *n*-hexane	Various temperatures, 400–630 K; 16 h *in vacuo*	0.5 g of support + 5 cm^3 of MCC solution, anhydrous, oxygen-free; up to 24 h; 293 K	0	If not oxygen-free, MCC adsorption ~35%
γ-Al_2O_3	$Ir_4(CO)_{12}$	0.4 mg cm^{-3} in cyclohexane (saturated solution)	380 K; 24 h *in vacuo*	0.5 g support + 50 cm^3 of MCC solution, anhydrous, 12 h; 293 K	100	
SiO_2	$Ir_4(CO)_{12}$	0.4 mg cm^{-3} in cyclohexane (saturated solution)	380 K; 24 h *in vacuo*	0.5 g of support + 50 cm^3 of MCC solution, anhydrous; up to 24 h, 293 K	<5	
γ-Al_2O_3	$Rh_6(CO)_{16}$	4 mg cm^{-3} in chloroform	380 K; 24 h *in vacuo*	0.5 g support + 10 cm^3 of MCC solution, anhydrous, oxygen-free; 24 h; 293 K	50	
SiO_2	$Rh_6(CO)_{16}$	4 mg cm^{-3} in chloroform	380 K; 24 h *in vacuo*	0.5 g of support + 10 cm^3 of MCC solution; anhydrous, oxygen-free; 24 h; 293 K	0	If not oxygen-free, MCC adsorption also zero
γ-Al_2O_3 or SiO_2	$Ru_3(CO)_{12}$	0.01 mg cm^{-3} in methylene dichloride (saturated solution)	380 K; 16 h *in vacuo*	0.5 g support + 20 cm^3 of MCC solution, anhydrous, oxygen-free; 3 h; 293 K	~10	MCC adsorption zero if pretreatment at 630 K

Chemicals. The $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ were prepared and purified according to the methods given by Martinengo *et al.* (*6*). The $Co_4(CO)_{12}$ was prepared and purified according to the method given by King (*7*). In these preparations, all handling and transfers were done under a dry nitrogen atmosphere.

Solvents and MCC Solutions

The experiments with the MCCs were carried out using solutions in nonaqueous solvents: *n*-hexane for $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, and $Co_4(CO)_{12}$; chloroform for $Rh_6(CO)_{16}$; cyclohexane for $Ir_4(CO)_{12}$; and methylene dichloride for $Ru_3(CO)_{12}$. All solvents were analytic reagent grade and were further purified by chemical drying, fractional distillation, and deoxygenation with a stream of pure, dry nitrogen. The concentrations of the MCC solutions were as indicated in column 3 of Table 1. All the cobalt-containing MCCs are oxygen sensitive, and the solutions of these MCCs were therefore prepared and stored under deoxygenated conditions: To be on the safe side, this was also done with solutions of $Rh_6(CO)_{16}$ and $Ru_3(CO)_{12}$. However, since $Ir_4(CO)_{12}$ is airstable, with this material this precaution was omitted.

Apparatus

(*i*) *Gas adsorption.* A standard all-glass volumetric apparatus was used, gas pressure being measured variously by U-tube mercury manometer or Pirani gauge. The gases (H_2 or CO) were spectroscopically pure grades.

(*ii*) *Electron microscopy.* A Phillips EM 200 or a Siemens 102 was used. Specimens were prepared by grinding under methylchloroform, followed by deposition of some of the suspension on a holey carbon film mounted on a copper grid. A standard anti-contamination device was used.

(*iii*) *Magnetic susceptibility.* Measurements were made by the Gouy method at temperatures in the range of 80–300 K and at field strengths up to about 10^6 A m^{-1}. Care was taken to obtain closely similar geometries for all unknown, calibration, and blank support specimens.

(*iv*) *Infrared measurements.* These were made using a Perkin–Elmer 577 spectrophotometer. Catalyst samples were examined after being pressed into a wafer (10–20 mg cm^{-2}) which was mounted in a cell (*8*) which allowed the wafer to be moved for processing at higher temperatures.

Metallic Cluster Carbonyl Adsorption onto Silica and Alumina

All adsorption measurements were made by agitation of a slurry of support and MCC solutions at room temperature, and the extent of MCC uptake onto the support was estimated colorimetrically. The results are summarized in Table 1. Results indicated as "not oxygen-free" refer to a situation where the support had been dried in air under the indicated conditions but had not been purged free of occluded air before being presented to the MCC solution. Results indicated as "oxygen-free" were obtained after thorough and exhaustive purging with pure, dry nitrogen.

Infrared Results for Adsorbed MCC

Infrared spectra in the carbonyl region were obtained for adsorbed $Co_2Rh_2(CO)_{12}$ and adsorbed $Ir_4(CO)_{12}$. These specimens were prepared by recovering the support sample containing the adsorbed MCC, which was then evacuated for about 1 h at room temperature to remove solvent, followed by pressing into a wafer. In the case of $Co_2Rh_2(CO)_{12}$, the specimen manipulations were carried out under nitrogen.

The solution ir spectra for $Co_2Rh_2(CO)_{12}$ and $Ir_4(CO)_{12}$ observed in the present work are given in Table 2 and agree extremely closely with the literature data (*5, 10*).

The main features of the ir data for these MCCs adsorbed on γ-alumina are summarized in Table 2. Detailed ir data for the $Ir_4(CO)_{12}$ system, giving the changes which occur with various thermal treatments, will be published elsewhere (*9*).

The ir spectral change recorded in Table 2 for the initial adsorption of $Co_2Rh_2(CO)_{12}$ on γ-Al_2O_3 was irreversible in the sense that treatment with carbon monoxide at about 200 Pa at room temperature caused no change attributable to the adsorbed MCC.

Preparation and Characterization of Dispersed Catalysts

Experiments were carried out to assess the possibility of generating dispersed metallic catalysts by using an impregnation/adsorption method with MCC solutions. For this purpose, both silica and γ-alumina supports were used with solutions of $Co_2Rh_2(CO)_{12}$ in *n*-hexane and of $Ir_4(CO)_{12}$ in cyclohexane. Sufficient solution was used thoroughly to wet the support, but was insufficient to produce more than a small amount of excess liquid. Following impregnation, the solvent was removed by evacuation at room temperature on a rotary evaporator. With $Co_2Rh_2(CO)_{12}$, handling and transfers were done under an atmosphere of pure, dry nitrogen: $Ir_4(CO)_{12}$ was handled without exclusion of oxygen.

TABLE 2

Infrared Data

Sample	ν_{CO}/cm^{-1}	Comments
$Co_2Rh_2(CO)_{12}$		
In hexane solution	2074 (vw), 2064 (s), 2059 (s), 2038 (m), 2030 (m), 1910 (sh), 1920 (w), 1885 (s), 1871 (s), 1855 (w)	
Initially adsorbed on γ-Al_2O_3	2077 (s), 2032 (m)	ir bands progressively removed on heating in an inert atmosphere >300 K, or on standing in air at room temperature
$Ir_4(CO)_{12}$		
In carbon tetrachloride solution	2071 (s), 2032 (s)	
Initially adsorbed on γ-Al_2O_3	2068 (s), 2025 (m), 2000 (sh)	ir bands progressively removed on heating *in vacuo* at 320–620 K; complete removal required heating in hydrogen at 620 K.

For further processing of the catalyst, one of the following alternatives was followed, viz., the catalyst was heated in a stream of nitrogen or oxygen at 100 kPa (catalysts from $Co_2Rh_2(CO)_{12}$) or *in vacuo* (catalysts from $Ir_4(CO)_{12}$) in the temperature range of 573–623 K for 4 h. This was followed by reduction in a stream of hydrogen (50 kPa) for about 15 h in the range 623–673 K, then by evacuation at the reduction temperature to better than 1 mPa.

For comparison with the behavior of $Co_2Rh_2(CO)_{12}$, a catalyst was also prepared by impregnation of the silica support with an aqueous solution containing equimolar concentrations of cobalt and rhodium. This solution was prepared from analytical reagent-grade $Co(NO_3)_2 \cdot 6H_2O$ and $RhCl_3 \cdot 3H_2O$. After impregnation, the water solvent was removed by air drying at 373 K for 24 h, followed by heating in a nitrogen stream and by hydrogen reduction as described above.

The catalysts so produced were characterized by gas adsorption, electron microscopy, and in the case of cobalt-containing catalysts, by measurement of magnetic susceptibility. Metal contents were checked by XRF analysis.

The data from gas adsorption measurements are given in Table 3. The listed uptake values for hydrogen and carbon monoxide refer to the pressure range 0.3–3 kPa, in which the uptake at 293 K was virtually independent of pressure and thus corresponds to a "saturation" region of the isotherm.

The results from electron microscopy and magnetic susceptibility measurements are given in Table 4 in terms of the average metallic particle diameters so obtained. Average metallic particle diameters were obtained from susceptibility data in both the low-field and high-field approximations using the standard procedures (*11*, *5*). They were evaluated using a value of 70 A m^2 kg^{-1} for the saturation magnetization of Co–Rh of equimolar ratio, this value having been obtained by a comparison with known data for the Co–Pt system (*12*)

TABLE 3

Gas Adsorption Data for Catalysts Prepared by MCC Impregnation

Catalyst	Pretreatment		Hydrogen reduction temperature (K)	Gas adsorption at 293 K and at 0.3–3 kPa[b] (10^{20} gas molecules/g of metal)	
	Environment	T (K)		H_2	CO
Co–Rh/γ-Al_2O_3[a] (1 wt% metal) from $Co_2Rh_2(CO)_{12}$	N_2	573	673	17.2	—
	O_2	573	673	22.0	—
Co–Rh/SiO_2 (1 wt% metal) from $Co_2Rh_2(CO)_{12}$	N_2	573	653	5.91	—
	O_2	573	673	8.06	—
Ir/SiO_2 (0.84 wt% Ir) from $Ir_4(CO)_{12}$	Vacuum	623	623	12.4	19.2
Ir/γ-Al_2O_3 (2.48 wt% Ir) from $Ir_4(CO)_{12}$	Vacuum	623	623	6.7	14.5
Ir/γ-Al_2O_3 (0.31 wt% Ir) from $Ir_4(CO)_{12}$	Vacuum	623	623	15.1	76.6

[a] Dry weight basis.

[b] Corrected for adsorption on the support.

and from an extrapolation of our own data to $H^{-1} \rightarrow 0$.

DISCUSSION

Metal Cluster Carbonyl Adsorption

The data in Table 1 show that, with $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$ and $Rh_6(CO)_{16}$, the MCC is much more strongly adsorbed on γ-alumina than on silica. In the case of $Ru_3(CO)_{12}$, the extent of adsorption on both γ-alumina and silica is quite low and there is little difference in the behavior of the two supports. Our adsorption observations with $Rh_6(CO)_{16}$ and $Ru_3(CO)_{12}$ are consistent with those reported by Smith *et al.* (*4*) and by Robertson and Webb (*3*), respectively.

The infrared data from $Co_2Rh_2(CO)_{12}$ show that with this MCC the main adsorption process on γ-alumina occurs with the removal of bridging carbonyl groups, evidenced by the removal of carbonyl bands at <2000 cm^{-1}. Adsorption was irreversible, and it is reasonable to conclude that carbonyl removal is associated with a chemical interaction between the MCC and the surface. Although it is possible that there is an adsorption precursor involving interaction of the MCC with a surface Lewis site via the oxygen of a carbonyl group—a process well known in systems such as metal carbonyl plus aluminum halide and known to occur preferentially at bridging carbonyl groups—this precursor, if formed at all, must be quite short-lived in the present situation since none of the expected infrared evidence (*13*) is observed (a large decrease in ν_{co} for the coordinating carbonyl and a sizeable increase in ν_{co} for the other carbonyls). We suggest therefore that the main adsorption process involves ligand exchange in which a bridging carbonyl is replaced by a group such as OH^- or O^{2-} in the γ-alumina surface. For comparison, carbonyl replacement processes are well established for MCCs involving nucleophilic ligands such as iodide ion (*14*). Inasmuch as OH^- is likely to be the dominant surface anion, this is likely to be the species involved in MCC bonding at the surface.

In the case of $Ir_4(CO)_{12}$ which contains only terminal carbonyl groups, the ir spectrum following initial adsorption showed only the presence of an additional band at 2000 cm^{-1} over and above the two bands observed in solution. By comparison, we note that an additional band at 2005 cm^{-1} is observed for solid $Ir_4(CO)_{12}$ (*10*). We conclude that the initial adsorption was essentially physical in nature with the molecule remaining intact. In this case, as evidenced by the observed decrease in the carbonyl band intensity, carbonyl group removal occurred above room temperature; that is, progressively at increasing temperatures in the range 320–620 K.

Taking these ir results from adsorbed $Co_2Rh_2(CO)_{12}$ and $Ir_4(CO)_{12}$ together, it is clear that bridging carbonyl groups are more easily displaced by thermal treatment than are terminal groups. Smith *et al.* (*4*) also observed that treatment of adsorbed $Rh_6(CO)_{16}$ with oxygen at room temperature resulted in the preferential removal of bridging carbonyl groups.

The much more facile MCC adsorption on γ-alumina than on silica may be a consequence of the greater ionicity of surface oxygen in γ-alumina which would make it a stronger nucleophile.

The effect of oxygen on MCC adsorption is probably due to an oxidative ligand replacement process of the type

$$M_n(CO)_m + [O]_s + \tfrac{1}{2}O_2 \rightarrow \{M_n(CO)_{m-1}[O]_s\} + CO_2, \qquad (1)$$

where $[O]_s$ is a surface species such as OH_s^- or perhaps O_s^{2-}. Reaction (1) is presumably driven to the right by the

TABLE 4

Co–Rh Catalysts

Catalyst	Mean metallic particle size, $\bar{d}$ (nm)			Metallic dispersion, D ($\equiv N_{(S)M}/N_{(T)M}$)	Surface mole fraction of cobalt[c] ($x_{(S)Co}$)
	H_2 ads	EM[a]	MS[b]		
Co–Rh/SiO_2 (1 wt% metal),[d] from $Co_2Rh_2(CO)_{12}$					
N_2 processed	2.8_3	2.8	2.8_5[e]	0.38	0.96–>0.99
O_2 processed	2.4_3	2.7	—	0.44	
Co–Rh/γOAl_2O_3(1 wt% metal), from $Co_2Rh_2(CO)_{12}$					
N_2 processed	1.3_2	1–1.5[f]	—	0.76	0.63– 0.64
O_2 processed	1.1_9		—	0.98	0.51
Co–Rh/SiO_2 (1 wt% metal) from cobalt nitrate and rhodium chloride					
N_2 processed	5.8_5	—	5.0[g]	0.16	0.97–>0.99

[a] Average diameter from electron microscopy.

[b] Average diameter from magnetic susceptibility.

[c] Range corresponds to the two limits used in the solution to Eqs. (3) and (4); see text.

[d] Dry weight basis.

[e] Listed value is mean of low-field (3.1 nm) and high-field (2.6 nm) values.

[f] Uncertainty due to limited resolution of individual particles.

[g] Listed value is mean of low-field (5.4 nm) and high-field (4.6 nm)

formation of carbon dioxide. Evidence for this was provided by the observation of an ir band at 1368 cm^{-1} which we attribute to symmetrical stretching in surface carbonate. Moreover, it was observed that after adsorption of $Co_2Rh_2(CO)_{12}$ on silica in the presence of (a little) oxygen, the infrared spectrum of the adsorbed species was similar to that produced with γ-alumina in the absence of oxygen; that is, the adsorbed species gave bands at 2070 and 2020 cm^{-1}.

It will be noted from the data in Table 1 that this propensity for augmented adsorption in the presence of oxygen is limited, under our experimental conditions, to the MCCs which contain cobalt, and this correlates with the known sensitivity of cobalt carbonyls for reaction with oxygen. However, given sufficient time, this behavior would probably occur with other types of MCCs: For instance, Smith *et al.* (*4*) observed that when $Rh_6(CO)_{16}$ on alumina was left to stand in oxygen for several days at room temperature, extensive oxidative removal of carbonyl ligands occurred. (We have observed similar behavior with $Co_2Rh_2(CO)_{12}$ adsorbed on alumina or silica.) We note that oxidative decarbonylation has been already reported for $[Co^{I}(CN)_2(PEt_3)_2CO]^-$ (*23*), while what may be the first stage, that is, the oxidation of a CO ligand to COOH, has been reported with $[Ir^{III}Cl_2(PR_3)_2(CO)_2]^+$ (*24*).

Gas Adsorption and Catalyst Characterization

We shall confine our attention to the apparent monolayer region of the isotherm to which the data in Table 3 refer. Interpretation of the gas adsorption data requires a knowledge of the monolayer chemisorption stoichiometry $[X_m(A)]$. Here we define $X_m(A)$ for a gas of molecular type A, as the average number of surface metal atoms at monolayer coverage needed for the adsorption of each A molecule.

In the case of hydrogen on iridium, it is then reasonable (*5*) to take $X_m(H_2) = 2$, that is, each surface iridium atom carries one hydrogen atom. However, in the case of cobalt–rhodium catalysts, there is the problem that, while it is reasonable to expect $X_m(H_2) = 2$ for rhodium (*5*), there is now strong evidence that this is not true for supported cobalt (*15, 16*): In this case the data show that under apparent monolayer conditions there is only one chemisorbed hydrogen atom for about every three surface cobalt atoms, so that $X_m(H_2) = \frac{2}{3}$.

Cobalt–Rhodium Catalysts

We proceed by constructing a model for the nature of the dispersed cobalt–rhodium which is internally selfconsistent for average metallic particle size measured electron microscopically and by magnetic susceptibility and for hydrogen adsorption data.

The main complications in the interpretation of data from these cobalt–rhodium catalysts lie in whether the metallic particles all contain equal proportions of the two metals, and in the question of surface enrichment by the component of lower surface energy.

It should be noted first of all that these metals form a continuous series of solid solutions across the entire composition range (*17*), so that from a thermodynamic point of view phase separation will not occur. We therefore take the view that catalysts prepared from $Co_2Rh_2(CO)_{12}$ will necessarily consist of metallic particles each with equal amounts of the two metals. In the case of the catalyst prepared by conventional impregnation from cobalt nitrate and rhodium chloride, we also believe this to be so, although the method of preparation makes the conclusion less secure. Nevertheless, in this case, the average metallic particle size was large enough for X-ray diffraction to be useful, and this failed to provide any evidence for the existence of more than a single metallic phase.

In order to estimate surface enrichments, we have used standard regular solution theory (*18*, *19*), modified as described by Wynblatt and Ku (*20*), to take into account the strain energy due to different atomic sizes of cobalt and rhodium.

In carrying out this calculation we used the following parameter values. Surface energies (*21*): γ_{Co} and γ_{Rh}, 2.37 and 2.74 J m^{-2}, respectively: mean area per mole of (100) alloy surface: 4.06×10^4 m^2 mol^{-1}; regular solution parameter: 9.4 kJ mol^{-1} (in the absence of experimental thermodynamic data for the cobalt–rhodium system, the regular solution parameter was estimated by parameterization from the heats of atomization, 440 and 578 kJ mol^{-1} for cobalt and rhodium, respectively); area per atom: 0.662×10^{-19} and 0.752×10^{-19} m^2 for cobalt and rhodium, respectively; volume per atom: 0.913×10^{-29} and 1.377×10^{-29} m^3 for cobalt and rhodium, respectively. Using the procedure described by Wynblatt and Ku (*20*) with values for the bulk and shear moduli of cobalt and rhodium (*22*), we estimate the elastic strain energy term as 10.3 kJ mol^{-1}.

Because of the uncertainty in the extent to which the elastic strain energy should contribute to the enthalpy change for surface enrichment, we have evaluated surface enrichment values in two limits: one with the elastic strain energy fully included and the other with it excluded. In computing surface compositions with small particles, account must be taken of the depletion of the bulk which accompanies surface enrichment, by applying the necessary mass balance criteria. We have therefore proceeded by iteration to a best fit in average particle diameter ($\bar{d}$), between $\bar{d}$ from hydrogen adsorption and $\bar{d}$ measured by other independent means (electron microscopy and magnetic susceptibility), the constraints being the satisfaction of the surface enrichment thermodynamic relations and the mass balance criteria. The results are given in Table 4.

Table 4 also lists corresponding values for the metallic dispersion, *D*, defined as $N_{(S)M}/N_{(T)M}$, the ratio of the number of metal atoms (Co + Rh) in the surface to the total number of metal atoms, and lists the corresponding surface compositions, $x_{(S)Co}$. The range of values listed for $x_{(S)Co}$ corresponds to the two limiting cases indicated above. However, because these ranges are relatively narrow, we list only midrange values of $\bar{d}_{(H_2\ ads)}$ and *D*. It may be noted that if ideal mixture theory is used to calculate surface enrichment, values for $x_{(S)Co}$ are only about 6% below the lower limits given in Table 4, while values for *D* and $\bar{d}_{(H_2\ ads)}$ are then about 5 and 2.5% above and below the listed values, respectively.

On the whole the model accounts well for the results, with the various $\bar{d}$ values being internally consistent to an acceptable level.

These data demonstrate the considerable advantage to be had in terms of better metallic dispersion, by generating the catalyst from $Co_2Rh_2(CO)_{12}$ rather than from a conventional impregnation procedure using aqueous solutions of cobalt nitrate and rhodium chloride. The data also show that the dispersion is considerably better on γ-Al_2O_3, on which $Co_2Rh_2(CO)_{12}$ is adsorbed, than on SiO_2, on which it is not adsorbed or only adsorbed to a very limited extent. This trend is to be expected if failure to adsorb leads to the generation of metallic particles via occluded solute. Finally, processing the catalyst in oxygen leads to a better dispersion than processing in nitrogen: The presence of oxygen presumably results in reduced particle mobility, leading to diminished aggregation.

Iridium Catalysts

Values for the iridium dispersion, *D*, ($N_{(S)Ir}/N_{(T)Ir}$) and average iridium particle

TABLE 5

Iridium Catalysts

Catalyst	Metallic dispersion, D ($\equiv N_{(S)Ir}/N_{(T)Ir}$) ($=N_{(S)H}/N_{(T)Ir}$)	Mean metallic particle size, $\bar{d}$ (nm)		$N_{(S)CO}/N_{(T)Ir}$
		H_2 ads	EM[a]	
Ir/SiO_2 (0.84 wt% Ir)[b] from $Ir_4(CO)_{12}$	0.79	1.4	1.7	0.61
Ir/γ-Al_2O_3 (2.48 wt% Ir) from $Ir_4(CO)_{12}$	0.43	2.5	N.A.	0.46
Ir/γ-Al_2O_3 (0.31 wt% Ir) from $Ir_4(CO)_{12}$	1.0	$\leqslant 1.1$	—[c]	2.44

[a] Average diameter from electron microscopy.

[b] Dry weight basis.

[c] No metallic particles observable.

size may be obtained from the hydrogen adsorption data using the monolayer chemisorption stoichiometry $X_m(H_2) = 2$, together with the area and volume per atom, $a_{Ir} = 0.769 \times 10^{-19}$ m^2 and $v_{Ir} = 1.42 \times 10^{-29}$ m^3. Values are listed in Table 5 together with corresponding electron microscopic data. On the whole the agreement is reasonable.

Table 5 also gives values for the ratio $N_{(S)CO}/N_{(T)Ir}$. For the catalysts containing 0.84 and 2.48 wt% iridium, the ratio $N_{(S)CO}/N_{(T)Ir}$ is in approximate agreement with the metallic dispersion D, indicating that on these catalysts the chemisorption stoichiometry for carbon monoxide $X_m(CO) \simeq 1$.

However, for the catalyst with composition 0.31 wt% iridium, the behavior was notably different. For this catalyst $D = 1.0$ but $N_{(S)CO}/N_{(T)Ir} = 2.44$. Bearing in mind that $D = 1.0$ is consistent with a range of particle sizes below a limit of about 1.1 nm in the case of iridium, and also noting that for this catalyst we failed to resolve any metallic particles electron microscopically (with an effective detectibility limit of about 0.6 nm), it is clear that the average iridium particle size was extremely small, certainly <1 nm. Since one would expect a range of particle sizes, it is reasonable to expect that some proportion of the iridium was retained as Ir_4 clusters. The question remains whether $N_{(S)CO}/N_{(T)Ir} = 2.44$ indicates that this proportion was substantial. Comparison with some results of Della Betta (*25*) for highly dispersed ruthenium catalysts suggests that the answer is probably in the negative. Della Betta studied the adsorption of hydrogen and carbon monoxide for average ruthenium particle sizes in the range of 1.1–2.5 nm (evaluated from hydrogen chemisorption data, and assuming $X_m(H_2) = 2$); the corresponding values for $N_{(S)CO}/N_{(T)Ru}$ were in the range of 2.3–3.8. Clearly, with a metal for which a molecular cluster carbonyl exists, e.g., $Ru_3(CO)_{12}$ in the case of ruthenium, $N_{(S)CO}/N_{(T)M}$ can approach a value characteristic of the MCC even though the metallic particle size may be rather larger than that existing in the MCC itself.

Taking the present results with those of Smith *et al.* (*4*) allows some summary comments to be made about the general conditions required for the generation and retention of highly dispersed metal from MCCs on catalyst supports.

The MCC should be molecularly dispersed over the support surface before extensive decarbonylation begins. This is most readily achieved if the MCC is molecularly adsorbed. Although the initial MCC adsorption may be relatively strong (with a probable chemical interaction as in the case of $Co_2Rh_2(CO)_{12}$ adsorption on γ-alumina), weaker adsorption may be sufficient (with a probable physical interaction as in the case of $Ir_4(CO)_{12}$ on γ-alumina). This initial adsorption may be assisted by the presence of oxygen.

We conclude that an important factor during catalyst genesis is to avoid the formation of MCC crystallites occluded in the support pores, and from which relatively large metallic particles can be formed during decarbonylation. The generation of a metallic particle from an MCC crystallite is undoubtedly a complex process, but it is reasonable to suppose that it will be assisted by the close proximity of MCC molecules in the crystallite, and that disproportionation reactions (well known for many MCCs) will probably play a significant role.

However, the behavior of $Ir_4(CO)_{12}$ on silica suggests that circumstances may exist when the absence of MCC adsorption need not necessarily lead to a poor metallic dispersion: in this case, at a metal loading of 0.84 wt% iridium, an iridium dispersion of 0.79 was obtained. This appears to be a result of events occurring during the early stages of catalyst processing. Although occluded MCC crystallites were formed when the solvent was removed under vacuum at room temperature, during the next stage of processing, which consisted of heating *in vacuo* at 370 → 620 K, there was clear evidence for MCC volatilization, and this resulted in its redistribution over the support surface. In this case of iridium, it appears that the MCC had sufficient volatility for redistribution to occur, but sufficient thermal lability for decarbonylation before any but a small amount (estimated by analysis at $<5\%$ of the total) of iridium was lost from the catalyst. This clearly requires a successful balance being struck between ease of volatilization and thermal decomposition, a fortuitous circumstance.

On the other hand, in the case of $Co_2Rh_2(CO)_{12}$ on silica where the MCC was also not adsorbed, the much greater thermal instability of this MCC relative to its volatility apparently prevented an analogous process from occurring: The result is that processing at 573 K (in nitrogen) resulted in $D = 0.36$; cf. Table 4. The relative ease of thermal decomposition of these MCCs as indicated above agrees with the literature: $Ir_4(CO)_{12}$, $T_d \simeq 480$ K; $Co_2Rh_2(CO)_{12}$, $T_d \simeq 390$ K (*6*).

Finally, we note the data of Smith *et al.* (*4*) which indicate that reversible decarbonylation/carbonylation is possible from $Rh_6(CO)_{16}$ adsorbed on alumina at room temperature, showing substantial absence of aggregation of the metallic skeletal units: decarbonylation without heating above room temperature must be carried out oxidatively (dry oxygen). Comparison with the present results suggests that an appreciable degree of aggregation of the MCC metallic skeletal units cannot be avoided if the catalyst processing temperature rises substantially above room temperature. However, even if heating above room temperature is avoided, reversible decarbonylation/carbonylation is not guaranteed, and depends on the specific MCC used. Thus the initial changes induced during the adsorption of $Co_2Rh_2(CO)_{12}$ on γ-alumina at room temperature were irreversible. The important factor is probably the strength with which the MCC is bound to the support.

Inasmuch as an MCC molecularly adsorbed on a 200 $m^2\ g^{-1}$ support to a metal loading of 1 wt% corresponds to an average intermolecular distance of the order of 5 nm, it is clear that aggregation from a molecularly dispersed MCC precursor must require considerable surface mobility. Carrying out the catalyst processing in the presence of oxygen gives a higher metallic dispersion, probably by reducing this surface mobility. It may be possible to achieve the same result by designing the support surface to make available surface sites of higher binding energy for the MCC.

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