

Noble Metals Supported on Phillips-Type Catalysts: Preparation, Characterization, and Activity for Ethane Hydrogenolysis

GEOFFREY C. BOND AND GERD HIERL¹

School of Chemistry, Brunel University, Uxbridge UB8 3PH, England

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Electron-transfer reactions between AgClO_4 , $\text{PdCl}_2(\text{PhCN})_2$ and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ dissolved in aprotic solvents (toluene or tetrahydrofuran) with Cr(II) ions on the surface of SiO_2 have been followed at room temperature, in the absence of air, and at various metal:Cr(II) ratios, by EPR spectrometry. A broad, intense signal characteristic of spin-coupled Cr(III) was generally observed, but the reactions proceeded neither stoichiometrically nor simply. When the molar Pd(II):Cr(II) ratio was 0.5 or less, most of the Pd(II) was reduced to Pd^0 by electron transfer from the Cr(II): when it was greater, the excess complex partly adsorbed and decomposed on the support. Oxidation of Cr(II) by electron-transfer to Rh(I) was however complete only when the Rh(I):Cr(II) ratio was 5. With AgClO_4 , the principal reaction was reduction of the anion, giving AgCl and $\text{Ag}_2\text{Cr}_2\text{O}_7$. Products after drying were characterized by X-ray diffraction, transmission electron microscopy, but most informatively by selective chemisorption (CO on Pd, H_2 on Rh) after reduction in H_2 at 120°C and evacuation at 380°C . The Pd metal area (expressed as m^2 per g metal) increased as the molar Pd(II):Cr(II) ratio was decreased from 2.5 to 0.18, where the Pd was monatomically dispersed ($\text{CO}/\text{Pd}_s \approx 1$). In the Rh-containing products, the Rh was only moderately well dispersed ($\bar{d} \sim 50\text{--}125 \text{ \AA}$). Pd^0 formed by electron-transfer from Cr(II) showed transient specific activity for ethane hydrogenolysis some 300 times higher than that shown by larger particles. Specific activities of the Rh catalysts were also about 100 times larger than previously reported values.

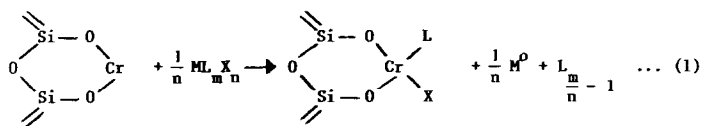
INTRODUCTION

Conventional preparations of supported metal catalysts usually begin either with the impregnation of a porous support with an aqueous solution of a salt of the metal, or with cation exchange of protons on the surface of the support by means of a suitable salt or complex, also from aqueous solution. There is then a drying step, sometimes followed by calcination, and finally the material is reduced, usually with H_2 , at the appropriate temperature. The mean size, size distribution, and location

within the support particles of the resulting metal crystallites are thus mainly governed by the pore structure of the support, or by the acidic characteristics of its surface, and by the mobility of intermediate species during drying, calcination, or reduction. Precise control over these factors is extremely difficult.

We have investigated an alternative route to the preparation of supported metals, using a support on which is incorporated a reducing function. A system with the desired properties is the CO-reduced Phillips catalyst, the reductant being coordinatively unsaturated Cr(II) bound to the SiO_2 support by two $\equiv\text{SiO}^-$ groups (1). Its reaction with a noble metal compound in a suitable solvent might occur as:

¹ Present address: Institut für Silicatiforschung, Neunerplatz 2, 87 Würzburg, West Germany.



where X^- is an anion and L is a solvent molecule or other ligand. Thus reduction of the metal by electron transfer from the Cr(II) should create first atomically dispersed metal on the surface, although subsequent diffusion and collision might lead to small crystallites. Assuming an even distribution of the Cr(II) centers over the surface, the average distance between them is calculated to be ca. 1.5 nm for the material used in this work. Since this procedure avoids the use of high temperatures, one would expect only limited mobility of metal atoms and consequently the formation of highly dispersed metal. In this paper we report (i) the preparation of Rh, Pd, and Ag catalysts, (ii) their characterization by EPR, X-ray diffraction, transmission electron microscopy, and specific H_2 or CO chemisorption, and (iii) the activity of the Rh and Pd catalysts for the hydrogenolysis of ethane.

EXPERIMENT

Materials. The preparation of Cr(II)/ SiO_2 (2.1 wt% total Cr, 1.8 wt% Cr(II), 3.5×10^{-4} mole Cr(II) g^{-1} , average oxidation state 2.14) has been described earlier (1). AgClO_4 (BDH, reagent grade) was dried at 130°C and 0.1 Torr for 5 h, and stored under Ar. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was supplied by Johnson Matthey Chemicals Ltd. and used without further purification. $\text{PdCl}_2(\text{PhCN})_2$ was prepared by Kharasch's method (2). Toluene and tetrahydrofuran (THF) were refluxed over Na/benzophenone and purged with purified Ar (1) for several hours before fractionation, and stored under Ar.

Preparation of the metal on Cr/ SiO_2 catalysts was carried out according to the following general procedure, which involved the application of Schlenk tube techniques

with Ar for all operations to maintain strictly O_2 -free conditions. A weighed amount of the metal compound was dissolved in the minimum volume of solvent after several vacuum/Ar cycles and then passed through a glass sinter to a magnetically stirred suspension of the Cr(II)/ SiO_2 (ca. 1 g in 25 ml solvent). The color of the solid gradually changed to black or brown. After stirring for several hours at room temperature, the liquid phase was removed by decantation and the solid washed with several portions of fresh solvent. The catalyst was then dried at 100°C by means of vacuum/Ar cycles for 30 min, and stored under Ar. Details of the preparations are given in Table 1.

Catalyst characterization. EPR spectra were recorded on a Varian E3 spectrometer in the X-band at room temperature: quartz sample tubes were fitted with Schlenk adapters to permit handling of materials under an inert atmosphere. X-Ray powder photographs were taken using an 11.46-cm-diameter camera and Ni-filtered CuK_α radiation, after exposure of the catalysts to air. Ultramicrotomed sections of catalysts embedded in Araldite were examined by transmission electron microscopy using an AEI E5 instrument.

Adsorption isotherms of H_2 on the Rh catalysts and of CO on the Pd catalysts were determined after the following pretreatment. Each sample was first evacuated overnight at room temperature (10^{-5} Torr); H_2 was then admitted (120 Torr) and the temperature raised to 120°C . After 1 h the H_2 was evacuated (16 h) and the temperature then raised to 380°C ; after 1.5 h (10^{-5} Torr) the sample was cooled to room temperature and the isotherm measured. Corrections were applied for the small amount of physical adsorption of CO on the pure

TABLE 1
Conditions of Catalyst Preparation

Number	Metal	Solvent	Metal taken (mmole)	M ⁿ⁺ /Cr(II) ^a	Reaction time (h)	Metal found (mmole)	Metal found (wt%)	Comments
1	Ag	H ₂ O	0.35	1	2.5	0.35	3.7	Immediate reaction: final washing with THF
2	Ag	THF	0.35	1	3	0.34	3.6	—
3	Ag	Toluene	0.35	1	3	0.34	3.6	Olive-brown product
4	Pd	THF	0.065	0.37	3	0.065	0.69	—
5	Pd	Toluene	0.175	1	3	0.176	1.87	—
6	Pd	THF	0.193	1.1	3	0.187	1.99	—
7	Pd	THF	0.35	2	3	0.255	2.71	—
8	Pd	THF	0.875	5	50	0.67	7.1	Partial decomposition of solution: no washing
9	Pd	THF	0.19	∞ ^b	0.5	0.19	2.02	Suspension evaporated to dryness <i>in vacuo</i>
10	Rh	THF	0.13	0.37	4.5	0.13	1.34	Dark olive-brown product
11	Rh	THF	0.35	1	3	0.24	2.48	—
12	Rh	THF	1.75	5	5	0.43	4.44	—
13	Rh	THF	0.284	∞ ^b	2.25	0.284	2.92	Suspension evaporated to dryness <i>in vacuo</i> : yellow-grey product

^a Ratio of equivalents initially present.

^b Cr-free SiO₂ support had undergone all stages of the Cr(II)/SiO₂ preparation, except impregnation with CrO₃ in H₂O.

support; physical adsorption of H₂ was negligible.

Measurement of catalytic activities. A mixture of C₂H₆ + H₂ (H₂/C₂H₆ = 6) was prepared by passing the appropriate mixture of C₂H₄ and H₂ over a Pd/SiO₂ catalyst at atmospheric pressure under conditions such that complete conversion to C₂H₆ occurred. Cylinder H₂ was purified by passage over Pd/Al₂O₃ pellets and 5A molecular sieve; cylinder C₂H₄ was merely passed over 5A sieve. The catalyst rested on a glass sinter in a Pyrex tube of 7 mm i.d. Products were analyzed by glc using a 30-cm column of Al₂O₃ at 50°C and N₂ as carrier gas; a flame ionization detector allowed the measurement of conversions to CH₄ as low as 0.005%.

To record the observed rapid changes in activity during the early stages of the use of these catalysts, the following conditions were used throughout. Catalyst (150 mg) was placed in the reactor, and the reactant mixture introduced at room temperature (total flow rate, 35 cm³ min⁻¹); after 5 min, the temperature was raised linearly (about 10 K min⁻¹) to either 213.5°C for the Rh catalysts or 357.5°C for the Pd catalysts. Product analysis was performed at 1-min

intervals from the onset of temperature programming: the appearance of CH₄ was first detected at 170°C over the Rh catalysts and at 220°C over the Pd catalysts.

RESULTS AND DISCUSSION

EPR Spectroscopy

EPR spectroscopy was used to investigate the oxidation states of Cr ions formed in the redox reactions between Cr(II) and the metal salt or complexes. The starting material itself showed only a weak asymmetric signal ($g \approx 4$) and a very weak symmetric signal ($g = 1.97$, $\Delta H_{pp} = 120$ G) (Fig. 1A). They have been ascribed to isolated (δ -phase) and spin-interacting (β -phase) Cr(III) ions, respectively (3). The double integrated δ -signal accounted for only about 2% of the Cr(III) present (based on the average oxidation number of 2.14), so the remainder was presumed to be of the β -type, giving too broad a signal to be detected. After oxidation with dry O₂ and subsequent evacuation, an intense and sharp asymmetric line appeared ($g = 1.97$) (Fig. 1B): this so-called γ -phase has been controversially attributed to single Cr(V) centers (3) as well as to spin-exchanging

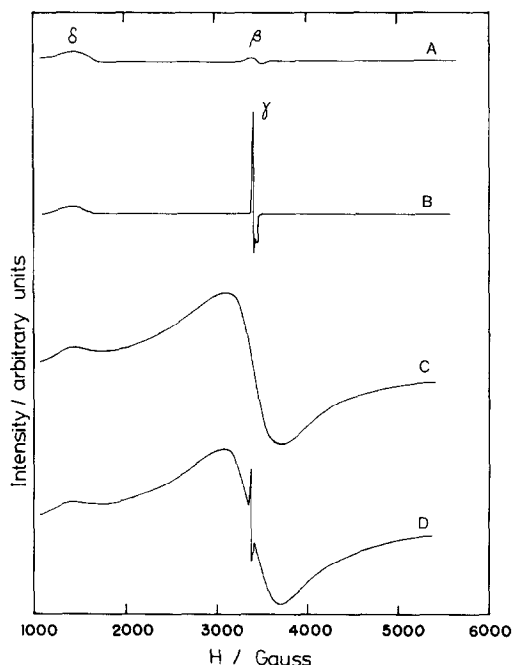


FIG. 1. EPR spectra of Phillips catalysts (A) After CO reduction, under Ar; (B) the same after admission of O_2 , under vacuum; (C) the same after reaction with $PdCl_2(PhCN)_2$ or $[Rh(CO)_2Cl]_2$, under vacuum; (D) after admission of O_2 to C, under vacuum.

Cr(VI)–Cr(III)–Cr(VI) triple centers (4). Counted as Cr(V) it represented about 1.9% of the total Cr; the main product of oxidation by O_2 is known to be diamagnetic Cr(VI) (5).

Experiments were performed in which the initial ratios of Pd(II) and of Rh(I) to Cr(II), expressed as equivalents assuming only the redox process to occur, were varied from 0.37 to 5; however with Ag(I) only equimolar ratios were used (Table 1). Oxidation of Cr(II)/ SiO_2 by solutions of either $PdCl_2(PhCN)_2$ or $[Rh(CO)_2Cl]_2$ produced a broad, very intense signal ($g = 1.97$, $\Delta H_{pp} = 500$ – 650 G) characteristic of spin-coupled Cr(III) (Fig. 1C): we therefore conclude that Cr(II) was oxidized to Cr(III) by electron-transfer of the noble metal. The solvents alone affected only the shape and intensity of the δ -signal, and did not cause any enhancement of the β -signal.

In those experiments where the ratio of equivalents of noble metal to Cr(II) was

greater than about unity (experiments 7, 8, 11–13 in Table 1), noble metal was found remaining in solution. After combining the filtrate and washings, and evaporation of the solvent, the amounts of the metals were estimated by standard procedures, and the amount of noble metal on the catalyst was found by difference. This procedure does not of course reveal the form of the metal remaining on the solid, or the nature of the process which led to its retention. Figure 2 illustrates the relationships between the initial ratio of equivalents, the noble metal content of the solid in $mequiv\ g^{-1}$, and the height of the Cr(III) signal in arbitrary units. Except in experiment 8, times of reaction were comparable, and variations seemed to have only a minor effect; for example, repetition of experiment 11 with a time of 5 h led to identical results.

In the Pd system, the Pd content of the catalyst was greater than the theoretical limit as determined by the Cr(II) concentration when the initial ratio of equivalents exceeded about unity (Fig. 2). Clearly some process other than the redox reaction (1) has led to retention of metal by the solid: one possibility is that the complex may decompose on the SiO_2 support itself, and

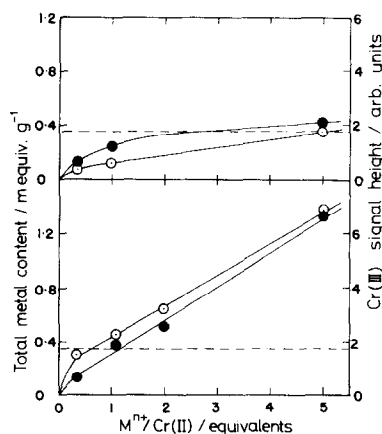


FIG. 2. Dependence of noble metal content of solid (solid points) and of Cr(III) signal height (open points) upon the initial ratio of M^{n+} to Cr(II). The broken lines represent the maximum amount of metal which may be formed by electron transfer. Upper diagram, Rh; lower diagram, Pd.

this was indeed confirmed by tests with Cr-free support. After treating SiO_2 for 3 h with a solution of $\text{PdCl}_2(\text{PhCN})_2$ in THF and then washing with the solvent, the SiO_2 appeared grey. Decomposition in solution to insoluble products was also observed in experiment 8. With Rh, the metal content did not much exceed the theoretical limit even when the initial ratio of equivalents was 5, but the Rh complex also reacted with Cr-free silica. The original yellow color of $[\text{Rh}(\text{CO})_2\text{Cl}]_2/\text{SiO}_2$ changed to a dirty greenish-yellow during evaporation of the solvent at 100°C (experiment 13), and slowly to brown when the sample was stored in air in a closed vessel. Another complication appears to arise from strongly adsorbed complex molecules being sufficiently mobile to react slowly with Cr(II) centers, as a further increase in the Cr(III) signal was observed in dry samples which had been stored under Ar for several months. That part of the complexes which is decomposed on the SiO_2 support, or which is merely retained through being strongly adsorbed, or which is precipitated after decomposition in solution, will probably be reduced to metal under the conditions employed in the chemisorption and catalytic experiments (see below). For convenience we refer to this as Type II metal, and that formed by electron-transfer as Type I metal.

In principle a plot of Cr(III) signal height versus total metal content should allow estimation of the fraction of retained metal which has been reduced in the redox process, viz. Type I/(Type I + Type II). We do not however know the form of the relationship between signal height and Cr(III) concentration for the spin-exchanging Cr(III) centers. If we assume proportionality and a theoretical maximum signal height somewhat greater than that observed in experiment 8, we can get an approximate idea of that fraction by simple projection. In Fig. 3 the solid line gives the size of the Cr(III) signal expected on these assumptions if process (1) occurs exclusively; the

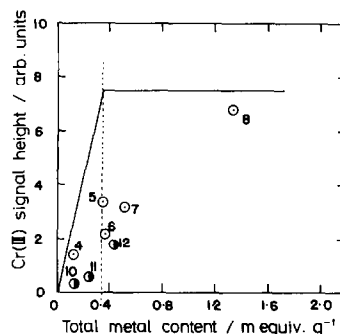


FIG. 3. Dependence of Cr(III) signal height on total metal content. The broken line represents the maximum amount of metal which may be formed by electron transfer; for further description, see text. Open points, Pd; half-filled points, Rh.

horizontal distance of any point from this line thus measures the amount of metal retained due to other factors (i.e., Type II metal).

We may summarize our conclusions from this part of the work as follows. There is clear evidence for the occurrence of electron-transfer between Cr(II) and Pd(II) or Rh(I) in the complexes, but the reactions do not proceed stoichiometrically according to process (1). In the Pd system, essentially complete utilization of the Cr(II) in the redox process occurs only when a considerable excess of the Pd(II) complex is present (experiment 8): then of course much (about $\frac{2}{3}$) of the Pd metal ultimately formed after treatment with H_2 is Type II (Fig. 3). On the other hand, when there is a stoichiometric deficiency of the Pd(II) complex (experiment 4), a larger fraction (about one-half) of the Pd in the catalyst is Type I. The Rh(I) complex seems to react less efficiently with Cr(II) than does the Pd(II) complex. Even where there is an excess of Cr(II) over Rh(I) (experiments 10 and 11), relatively little Type I Rh metal results, as shown by the low Cr(III) signal. Moreover the total Rh content of the solid does not rise in proportion to the amount of the Rh(I) complex taken, in contrast to the situation with Pd, perhaps because the SiO_2 surface has only a limited ability to retain or to decompose the Rh(I) complex. However the *frac-*

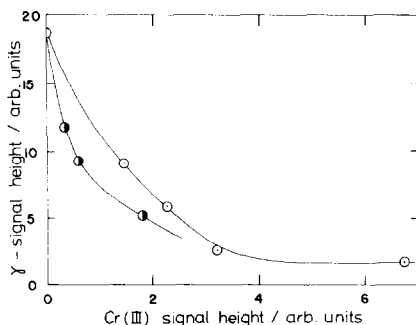


FIG. 4. Dependence of γ -signal height on Cr(III) signal height. Symbols as in Fig. 3.

tion of Cr(II) utilized in reducing it to the metal does appear to increase with increasing Rh(I):Cr(II) ratio (Figs. 2 and 3). Thus in both systems the ratio of Type I to Type II metal decreases with increasing metal content, because the electron-transfer reduction of the complexes is more probable when Cr(II) is in excess.

The Pd and Rh catalysts were at this stage still sensitive to oxidation by O_2 . After admission of O_2 to 1 atm and subsequent evacuation, the EPR spectra exhibited an additional γ -signal (Fig. 1D) and in most cases a slightly increased Cr(III) signal. The heights of these two signals showed an interesting correlation with each other (Fig. 4). Under the preparation conditions used, the formation of the γ -phase was not noticeably suppressed by THF and only to about 15% by PhCN in THF at a concentration corresponding to that used in preparation 8. We therefore conclude that the Cr(II) unconsumed by process 1 could be oxidized by O_2 to that Cr species responsible for the γ -signal. Provided that the height of the Cr(III) signal is proportional to the number of Cr(III) centers, the nonlinearity of the plots in Fig. 4 provides further evidence (6) that the Cr(II) centers are nonuniform with respect to oxidation to the γ -phase.

Reaction of $AgClO_4$ with Cr(II)/ SiO_2

With water as solvent, the anion was immediately reduced, and this was the

only observable reaction: it occurred at least in part homogeneously, since the Cr(II)—O—Si/ bonds were hydrolytically cleaved. The resulting catalyst was still slightly sensitive to oxygen. In the aprotic solvents THF and toluene, reduction of the anion was a competing side-reaction. Surprisingly, the EPR spectra exhibited both the Cr(III) and the γ -signal, and the latter did not increase on exposure to O_2 . The X-ray diffraction pattern of the resulting olive-brown solid matched the most intensive reflections of $AgClO_2$, $AgCl$, and $Ag_2Cr_2O_7$, the lines due to the first being much weaker than those of the others. $AgClO_2$ and $AgCl$ are reduction products of $AgClO_4$ formed in four-electron steps: thus in contrast to the one-electron reductions of Pd(II) and Rh(I) in which Cr(II) is oxidized to Cr(III), in the reduction of ClO_4^- the Cr(II) is apparently oxidized directly to Cr(VI). The insoluble $Ag_2Cr_2O_7$ clearly results from the interaction of $AgClO_4$ with surface $Cr_2O_7^{2-}$ ions.

Physical Characterization of Catalysts Containing Rh and Pd

The black appearance of the solid products and the observation of the Cr(III) EPR signal are of course only indirect evidence of the formation of elementary metal. We consider now the information obtained from X-ray diffraction (XRD), transmission electron microscopy (TEM), and selective chemisorption (SC) experiments. Our findings are summarized in Table 2.

Positive detection of elementary metal by XRD is only possible providing the average particle size exceeds about 50 Å and the metal concentration is above about 1%. The absence of detectable lines in the products of preparations 5, 6, 10, and 11 suggests that most of the metal was highly dispersed in these cases. With TEM we estimate that particles smaller than about 25 Å could not be identified with certainty against the background of the support. Excluding the Cr-free preparations, particles were clearly observed only in preparations

TABLE 2
 Characterization of Catalysts

Number	X-ray diffraction	Particle size ^a by TEM (Å)	Selective chemisorption			
			Adsorbate	n_m^s at $P = 0/\mu\text{mol}$ (mg metal) ⁻¹	Area/m ² (g metal) ⁻¹	Average size (Å)
1	Ag ^o	25–80 (60)	—	—	—	—
2	Ag ^o , AgCl, Ag ₂ Cr ₂ O ₇	25–70; 150–300	—	—	—	—
3	AgCl, AgClO ₂ , Ag ₂ Cr ₂ O ₇	80–160	—	—	—	—
3 ^b	Ag ^o	—	—	—	—	—
4	—	n.d.	CO	9.90, 9.13	941, 868	5.3, 5.7
5	—	n.d.	CO	3.78	359	14
6	—	n.d.	—	—	—	—
7	Pd ^o	70–150 ^c	CO	3.32	315	16
8	Pd ^o	25–150 (70)	CO	1.51	140	36
9 ^b	Pd ^o	25–100 (100)	CO	0.855	77.6	64
10	—	n.d.	H ₂	0.110	95.4	51
11	—	n.d.	H ₂	0.635, 0.867	53.9, 68.4	90, 71
12	<i>d</i>	200 ^c	H ₂	1.02	88.5	55
13 ^b	Rh ^o	25–70 (70)	H ₂	0.44, 0.43	39.3, 38.9	123

^a Size range; predominant size in parentheses. n.d. = no particles detected.

^b Catalysts pre-reduced in H₂ before examination: no. 3, 2 h at 410°C; no. 9, 3 h at 360°C; no. 13, 2.5 h at 155°C.

^c Very few particles visible.

^d Two very weak reflections observed, attributable to [Rh(CO)₂Cl]₂, although the d-spacings are not those of the most intense lines.

7 and 8, these being the ones expected to have a high ratio of Type II to Type I metal. Even when observed, particles were not sufficiently numerous for estimation of a size distribution, and the size ranges and dominant sizes given in Table 2 are only approximate: the observable particles may only be a small fraction of the total.

To obtain further information on the particle size of the metal, we measured the adsorption isotherms for CO on most of the Pd catalysts, and for H₂ on the Rh catalysts (see Table 2). The dangers inherent in doing this are, first, that it is necessary to pre-reduce with H₂ and then to outgas in order to produce a clean surface for chemisorption, and this treatment may produce other metal particles than those formed in the initial redox process, i.e., Type II metal. Second, evacuation at 380°C for 1.5 h may cause sintering of the metal particles, which it was the object of our procedure to avoid. Third, it is possible that some chemisorp-

tion will occur on the Cr(III) or other Cr species also present at the surface.

A selection of the isotherms is shown in Fig. 5. Those for the Cr-free catalysts have an acceptably low slope between 10 and 20 Torr, and hence the volume adsorbed at zero coverage can be estimated quite accurately. However, this is evidently not so for the Cr-containing Rh catalysts, where the higher slopes in the region of 10 Torr suggest that an additional and weaker chemisorption of H₂ is occurring, perhaps on the Cr centers. Nevertheless by extrapolating the tangents at 10 Torr to zero pressure and thus deriving values of the monolayer capacity n_m^s , reasonable estimates of the amounts of chemisorption on the Rh surface are perhaps obtained. The values for the areas and particle sizes given in Table 2 were derived using $H/Rh_s = 1$ and the uniform sphere approximation (7). The isotherms for CO on the Cr-containing Pd catalysts had less steep slopes between 10

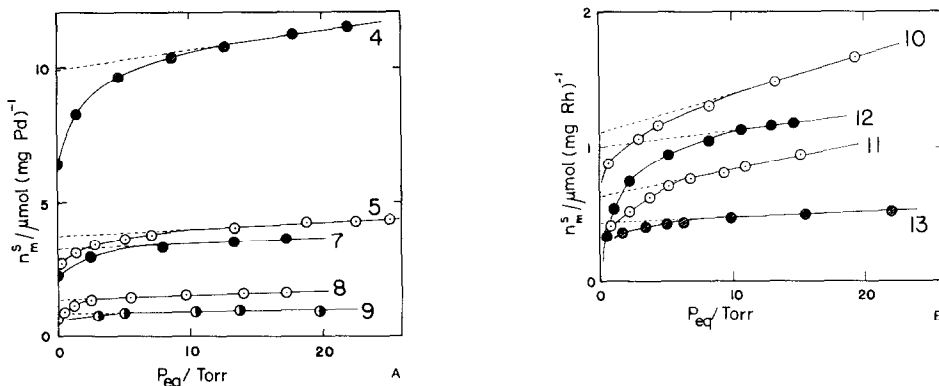


FIG. 5. Adsorption isotherms for (A) CO on Pd-containing samples and (B) H₂ on Rh-containing samples. The numbers refer to the various preparations (see Tables 1 and 2 for details).

and 20 Torr (Fig. 5), and the values of n_m^s can be reliably estimated. The value of CO/Pd_s appears (8) to vary between unity and 0.5 (i.e., from pure linear to pure bridged forms) depending on the support and perhaps even on the particle size. Since trends are of more importance in this work than absolute values, we have used CO/Pd_s = 0.5 throughout, and again the uniform sphere model to obtain particle sizes.

The estimates of Pd particle size given in Table 2 support our contention that Type I metal formed in the redox process is more highly dispersed than the Type II metal formed without the help of Cr(II), since the particle size decreases almost linearly with decreasing Pd : Cr ratio. The monolayer capacity of the product of experiment 4 was so surprisingly high (almost 10 μmole per mg Pd) that the measurement had to be repeated, but the second result agreed quite closely with the first (see Table 2). The significance of particle size diminishes with its magnitude, and no real meaning can be attached to the derived values of 5.3 and 5.7 Å. The amount of CO expected to be chemisorbed if one CO molecule were attached to every Pd atom is 9.4 μmole per mg Pd, a value which is close to the mean of the two observations (9.5 μmole mg⁻¹). Thus even if the CO were purely bridged when adsorbed on this catalyst, we should still conclude that the metal is effectively

100% dispersed either as aggregates or islands one atom thick, or monatomically dispersed. Highly dispersed metal can thus apparently withstand the effects of the rigorous outgassing procedure employed. The results for the rhodium catalysts (Table 2) confirm our suspicion that the extent of the redox process is not as large as in the Pd-containing preparations.

Catalytic Activity in Ethane Hydrogenolysis

The activity of selected Pd- and Rh-containing catalysts for ethane hydrogenolysis was briefly examined. This reaction was chosen because it is known to be structure-sensitive (at least for Rh catalysts (9)), and thus the effects of any highly dispersed metal present might be easily seen. Against the possibility of rapid sintering and loss of activity, conversion was measured at 10 K intervals during the heating period. Results of a typical experiment with a Pd catalyst are shown in Fig. 6. The most striking feature is the activity maximum in the heating period, caused by the onset of deactivation before the final temperature was attained. The results for the other Pd and Rh catalysts are shown in Figs. 7 and 8; rates were calculated from the expression

$$r = (F/W)c$$

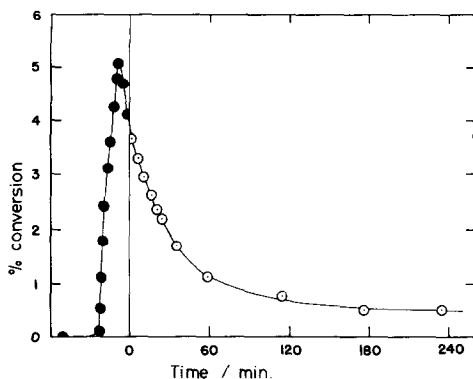


FIG. 6. Hydrogenolysis of ethane using Pd preparation no 6: variation of rate with time. The filled points were obtained during the heating period, and the open ones at 357.5°C.

where F is the flow rate of C_2H_6 in mole h^{-1} , W the weight of Pd or Rh in the reactor in g, and c the fraction of C_2H_6 converted to CH_4 . Conversion to units of molecules $cm^{-2} s^{-1}$, to facilitate comparison with the results of other workers, was performed using the areas (or average areas) quoted in Table 2. Rates measured during the heating periods and plotted in Figs. 6 to 8 have been adjusted to the reaction temperatures (357.5°C for Pd and 213.5°C for Rh) using apparent activation energies of, respectively, 243 and 185 kJ $mole^{-1}$ determined after activities had stabilized (see Table 3). The rates of deactivation of the Cr-containing Pd catalysts during the earlier part of the heating periods were sufficiently low to permit derivation of a meaningful activation energy from the dependence of conversion on temperature, and hence pre-exponential factors and rates at an arbitrarily chosen temperature of 205°C. The results, together with those obtained from steady-state measurements and some literature (9, 10) values are presented in Table 3. Comparing first our steady-state results with those in the literature, the agreement on activation energies is very satisfactory: for Pd catalysts our steady state rates agree very well with Sinfelt's (10) but our Rh catalysts appear to be at least 100 times more active than his most active. There is no clear explanation

for this, since although there is known to be a marked specific particle size effect (9), our particle sizes are not in the range where Sinfelt finds highest activities (12 to 41 Å).

We examine now the non-steady-state behavior of our catalysts. The Cr-free Pd catalyst (no. 9) was perfectly stable (Fig. 7); for the Cr-containing catalysts, the maximum activity shown during the heating period was inversely related to the Pd:Cr ratio and was thus approximately proportional to metal area (see Table 2). The extent of activity loss, i.e., the ratio of the maximum rate to the rate after 2 to 4 h at temperature, was also inversely related to the Pd:Cr ratio, and the rates after 2 to 4 h on stream were thus *inversely* related to the areas (Fig. 7). We can only speculate on the cause of the activity loss, but a likely explanation is the formation of toxic carbonaceous deposits about the particles. The picture which emerges is that the ultrasmall particles (<15 Å) are initially extremely active for hydrogenolysis (up to 2.7 decades more active than Cr-free catalysts). There is evidence (11) to show that particles of this size become electron-deficient through electron transfer to the support, and hence partake of some of the character

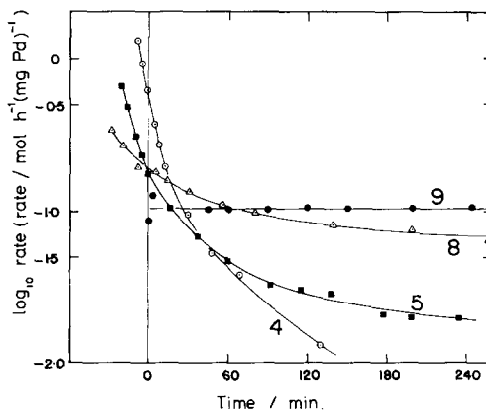


FIG. 7. Time-dependence of activity of various Pd-containing samples for ethane hydrogenolysis. Points to the left of the vertical line (zero time) were obtained during heating, those to the right at 357.5°C. The numbers refer to the preparations listed in Tables 1 and 2. In this and in Fig. 8, a number of experimental points have been omitted for the sake of clarity.

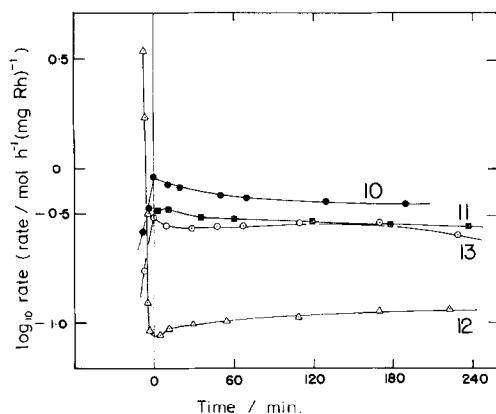


FIG. 8. Time-dependence of activity of various Rh-containing samples for ethane hydrogenolysis. The notes in the legend to Fig. 7 also apply here, except that the constant temperature was 213.5°C.

of the element immediately to the left in the Periodic Table: Rh is of course much more active than Pd for ethane hydrogenolysis (10). In this connection it is of interest that the activation energy exhibited by the very well-dispersed Pd preparation no. 4 (191 kJ mole⁻¹) is more akin to the values shown by the Rh catalysts (~185 kJ mole⁻¹) than by the other less well-dispersed Pd catalysts (~230–260 kJ mole⁻¹). Such ultrasmall particles, however, contain the seeds of their own destruction, for this hyperactivity is only short-lived. We have the impression that *all* the Type I metal present is deacti-

vated in the space of a few hours, and that the residual activity is solely due to the larger particles of Type II metal. This conclusion follows from the activities of the Pd catalysts after 2 to 4 h, which increase in proportion to the fraction of Type II metal likely to be in them (assuming the Cr-free catalyst 9 has only "Type II" metal). We cannot of course entirely discount the possibility that high initial activity and rapid deactivation is directly due to the oxidized Cr species present on the surface, or to collaboration between them and highly dispersed Pd, but both seem unlikely. We have seen no evidence for the formation of Pd–Cr alloys or clusters.

In contrast, the Rh catalysts did not in general show maxima in activity in the heating period, nor did they hence change much in activity after attaining a steady temperature (see Fig. 8). The exception is catalyst 12, which exhibited a very high activity in the heating period; this was the only Rh catalyst to show a substantial Cr(III) EPR signal due to the one-electron redox reaction Cr(II)/Rh(I) to Cr(III)/Rh(0), and hence may be the only catalyst to contain much Type I metal. The surface area measurements (Table 2) give some support for this view; the other Rh catalysts (especially nos. 11 and 13) are rather poorly dispersed.

TABLE 3
Arrhenius Parameters for C₂H₆ Hydrogenolysis

Catalyst	E(kJ mole ⁻¹)	log A ^a	log r ^a	log r _{max} ^a	Comments
0.69% Pd (no. 4)	191	29.36	8.46	13.41	Derived from heating period
1.99% Pd (no. 6)	262	35.68	6.88	13.48	Derived from heating period
1.99% Pd (no. 6)	244	32.17	5.47	—	After 6 h reaction
7.1% Pd (no. 8)	231	32.85	8.05	13.61	Derived from heating period
2.0% Pd (no. 9)	250 ^b	33.35	5.85	13.34	Catalyst in steady state
10% Pd/SiO ₂ ^c	262	33.57	5.72	—	Ref. (9)
2.48% Rh (no. 11)	182	33.68	13.68	—	After 6 h reaction
2.92% Rh (no. 13)	187	34.55	13.95	—	After 4 h reaction
5% Rh/SiO ₂ ^c	175	31.76	11.56	—	Ref. (9)

^a Units of A, r, and r_{max}, molecules cm⁻² s⁻¹; r calculated at 205°C.

^b Value assumed to calculate r at 205°C.

^c Rates measured with P_{C₂H₆} = 0.03 atm, P_{H₂} = 0.2 atm.

An Ag catalyst (no. 3) did not show any activity for ethane hydrogenolysis at temperatures up to 410°C.

CONCLUSION

Evidence has been presented to show that an electron-transfer reaction can occur between coordinatively unsaturated Cr(II) ions on the surface of SiO₂ and PdCl₂(PhCN)₂ in nonhydroxylic solvents and in the absence of air to give atomically dispersed Pd, although the reaction is only stoichiometric when the Pd:Cr ratio is sufficiently low, and side-reactions leading to less well dispersed Pd also take place. Very highly dispersed Pd is extremely active for ethane hydrogenolysis, but the activity is unstable. The reaction of Cr(II) ions with [Rh(CO)₂Cl]₂ takes place less readily.

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