JOURNAL OF CATALYSIS **123**, 113–129 (1990)

The Formation of Supported Bimetallic Catalysts

II. The Application of a Quantitative DSC Technique

BAHMAN REJAI[1] AND RICHARD D. GONZALEZ[2]

Department of Chemical Engineering, University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680

Received February 16, 1989; revised December 12, 1989

In the first part of this study, we developed a quantitative technique using differential scanning calorimetry (DSC) to measure the enthalpies of various gas–solid reactions. This technique has been applied to the reduction reactions of unsupported and supported Pt and Ru precursors. The mechanisms of these reductions were investigated by measuring temperatures, enthalpies, and weight losses during the reduction process. The effect of the support was evaluated by considering changes in temperatures and enthalpies of reduction upon supporting on silica. The reduction of pure $RuCl_3$ occurs by a simple one-step reduction process. A complex mechanism is observed for the reduction of pure H_2PtCl_6. The reduction behavior of the supported precursors is in agreement with complex Ru surface speciation and the formation of $PtCl_4$ as an intermediate in the reduction process. Air-dried samples suggest the formation of $PtCl_4$ as a surface species prior to reduction. All bimetallic clusters were found to have an exothermic enthalpy of clustering.

INTRODUCTION

Thermal techniques such as temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), and temperature-programmed desorption (TPD) have been employed for many years in the characterization of catalysts used in heterogeneous catalysis. Unfortunately a great deal of information obtained through the use of these techniques has been qualitative rather than quantitative in nature. Additionally, there has been very little effort directed at measuring the enthalpies of reduction and decomposition of the supported precursors used in catalyst synthesis. Because these enthalpies may provide direct information regarding metal precursor–support interactive energies, we are of the opinion that such enthalpy measurements should provide a more complete description of supported mono- and multimetallic catalysts.

In a previous study (*1*), we reported on the development of a quantitative differential scanning calorimetry (DSC) technique which could be used to obtain precise enthalpy measurements for gas–solid reactions. The mathematical formulation of the relevant heat transfer equations in addition to the required thermal conductivity and hydrogen concentration extrapolations were considered in detail.

Using this technique, enthalpies for the decomposition of $CaC_2O_4 \cdot H_2O$ and for the reduction of PtO_2 and $PtCl_2$ were obtained. These enthalpies were in good agreement with values based on standard enthalpies of formation reported in the literature (*2, 3*). In this paper we present an extension of this technique to the study of the reduction of Pt and Ru precursors supported on silica. In addition, we will present quantitative measurements of reduction enthalpies which occur as the result of a bimetallic coassisted

---

[1] Present address: Solar Energy Research Institute, Golden, CO.

[2] To whom correspondence should be addressed.

0021-9517/90 $3.00

reduction process. The concepts and methods presented in this study can be generalized to include any monometallic or bimetallic system of interest.

In the preparation of supported bimetallic clusters it has generally been thought that the metal which has the lower enthalpy of sublimation is preferentially enriched at the surface (*3*). Although this has been found to be the case for a large number of supported bimetallic clusters, there is now a growing body of evidence which suggests that the surface diffusion of the metal precursor species during pretreatment is also important (*4–7*). Metal precursor species which interact weakly with the support may be expected to diffuse rapidly across the surface during catalyst pretreatment. Using these arguments, Gonzalez and co-workers (*4–6*) and Augustine *et al.* (*7*) have shown that the surface composition of the resulting bimetallic clusters is enriched in the metal whose precursor shows the greater mobility. In a recent study, Miura (*8*) has shown that changing the precursor from $RuCl_3 \cdot nH_2O$ to Ruthenocene (bis (cyclopentadienyl) ruthenium, $(C_5H_5)_2Ru$) can cause a reversal in the surface composition of supported Pt–Ru bimetallic clusters. For this reason, quantitative measurements of the interactive enthalpies between a metal precursor and its support become an important characterization parameter to predict preferential surface enrichment. Because thermodynamic phase equilibria is not usually achieved under the moderate pretreatment temperatures normally used, thermodynamic phase diagrams are less reliable as surface composition predictors than precursor–support interactions. However, this does not mean that they are not important. For example, Cu and Ru are completely immiscible in the bulk. When Cu and Ru are used to prepare supported Cu–Ru bimetallic clusters, Cu invariably segregates to the surface to form Cu islands or is preferentially located at centers of low surface coordination (*9–13*).

For the case of weak metal precursor–support interactions, the enthalpy of reduction should approach that of the pure metal precursor in the absence of the support. When the metal precursor interacts strongly with the support, the enthalpy of reduction will be considerably different from that of the pure precursor. In addition, it may be possible that variations in pretreatment, such as precalcination or drying in air at moderate temperatures, may have a profound effect on the structure of the precursor which is ultimately reduced (*14*). For this reason, variations in catalyst pretreatment conditions should be an important variable to be considered in the preparation of supported bimetallic clusters.

The preparation of supported $Pt–Ru/SiO_2$ bimetallic clusters was chosen for this study because of the large amount of data which has been obtained on this combination of metals (*4–6, 15*). We think that $RuCl_3 \cdot nH_2O$ interacts strongly with silica and that $H_2PtCl_6 \cdot mH_2O$ interacts weakly due to the anionic nature of the interaction (*4–6, 16*).

In order to predict the reduction mechanism of a metal precursor, a knowledge of the aqueous speciation chemistry and the stability of the pure precursor in addition to the interaction between the precursor and the support is necessary. Results on the reduction of Pt and Ru precursors available in the literature are limited and even contradictory in some cases. Some differential thermal analysis (DTA) (*17–19*) and temperature-programmed reduction (TPR) (*20, 21*) studies on supported Pt precursors have appeared in the literature. However, these studies were mostly qualitative in nature and no attempt was made to measure the enthalpies of reduction. Additionally, most of these studies were performed with large amounts of sample (30–170 mg), resulting in mass and heat transfer effects. Although either one or two reduction peaks for $H_2PtCl_6 \cdot mH_2O$ have been reported, the complete identification of the reduction sequence has not been achieved. Results on the reduction of $RuCl_3 \cdot nH_2O$ are even more scarce. To our knowledge a thermal gravimetric analysis study (TGA) performed by Newkirk and McKee (*22*) represents the only attempt at understanding the reduction sequence of $RuCl_3 \cdot nH_2O$.

EXPERIMENTAL

Catalyst preparation. The silica-supported samples used in this study were prepared by direct impregnation of silica by the incipient wetness technique. The metal precursors used were H_2PtCl_6 (hydrated, 38.84% Pt) and $RuCl_3$ (hydrated, 42.0% Ru). They were obtained from Strem Chemicals Co. (Newburyport, MA). The silica support was a Cab-O-Sil M-5 (Cabot Corp., Tuscola, IL) with a reported surface area of 200 m^2/g and an average pore size of 14 nm. The precursors were dissolved in an amount of doubly deionized water sufficient to ensure the complete wetting of the support. Total metal loadings were kept constant at 0.3 mmoles/g of silica for both the monometallic and bimetallic catalysts (~3–5% metal content). Two sets of catalysts were prepared using different drying procedures. The first set was dried in a vacuum desiccator at room temperature while the second was dried in flowing air at 150°C. Surface compositions for both sets of catalysts were measured using an O_2–CO titration technique (*4*). These results have been reported in a previous study (*16*).

Gravimetric analysis. Weight measurements were performed to an accuracy of 0.05 mg using a Sartorius electronic microbalance with a precision of 0.1 mg. For a sample of an initial weight W_0 and a weight loss of ΔW, the weight change ratios ($\Delta W/W_0$'s), are of an accuracy of $(2\alpha W_0 - \alpha \Delta W)/W_0^2$, where $\alpha = 0.05$ mg.

Energy dispersive X-ray spectroscopy. These measurements were carried out under vacuum using a Phillips PV-9550 EDXS equipped with a Rh X-ray tube at an accelerating voltage of 20 keV. Ratios of peak intensities were referenced to silicon in order to compute changes in the chlorine concentration of the samples.

RESULTS

Unsupported $RuCl_3$. The reduction of anhydrous $RuCl_3$ proceeds according to the following stoichiometric equation:

$$RuCl_3(s) + \tfrac{3}{2} H_2(g) \rightarrow 3HCl(g) + Ru(s) \qquad (1)$$

The experimental weight loss ratio $\Delta W/W_0 = 0.528 \pm 0.020$ was in good agreement with the weight loss ratio of 0.509 predicted by Eq. (1). This suggests complete reduction of Ru to the zero valent state.

The enthalpy of reduction of $RuCl_3$ was determined using the procedure outlined in Ref. (*1*). The reduction temperature was determined by extrapolation to zero H_2 concentration as shown in Fig. 1. These experiments were performed using a constant sample weight (1.4 mg). The heating rate was 10°C/min and the flow rate was 31.8 ml/min. The reduction temperature calculated by this method was found to be 187°C. From this result, the boundary layer temperature was calculated to be 107.5°C, the arithmetic average of the reduction and the purge gas temperatures (*1*).

The effect of thermal conductivity on the enthalpy of reduction is shown in Fig. 2 for five different hydrogen concentrations (0.5, 1.0, 1.5, 2.5, and 5.0%). In these experiments, the purge gas flow rate (31.8 ml/min), the heating rate (10°C/min), and the sample size (1.4 mg) were kept constant. The thermal conductivity was controlled by varying the composition of the purge gas consisting of H_2, He, and Ar. The thermal conductivity of the gas mixture was calculated using the method of Wassiljewa (*23*).

For each concentration of H_2, the measured energy change due to reduction was obtained by extrapolating the enthalpy of reduction to that corresponding to the thermal conductivity of HCl (g) calculated at the temperature of the boundary layer. The true value of the enthalpy of reduction was then calculated by plotting these values versus H_2 concentration and extrapolating to an infinite dilution of the purge gas with H_2, i.e., zero H_2 concentration. A least-square sec-

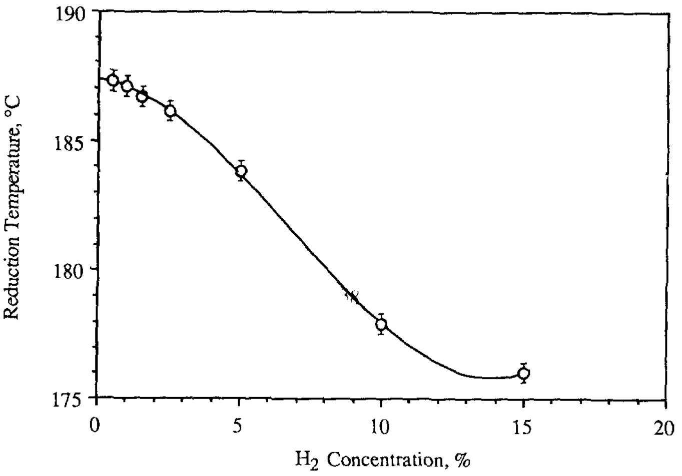

FIG. 1. The effect of H_2 concentration on the reduction temperature of $RuCl_3$.

ond-order polynomial curve fitting was used for this extrapolation. The results, shown in Fig. 3, lead to a reduction enthalpy of −29 ± 2 kJ/mole, in good agreement with the literature value of −23.0 kJ/mole (*2*). Experiments carried out using either pure He or N_2 showed that decomposition of $RuCl_3$ did not occur at temperatures of up to 500°C.

Supported $RuCl_3$. The reduction temperature of $RuCl_3/SiO_2$ was determined by extrapolating the reduction temperature vs hydrogen concentration curve to zero H_2 concentration in a manner which was analogous to the procedure followed in determining the reduction temperature of unsupported $RuCl_3$ (Fig. 4). A reduction temperature of 163°C was obtained for the vacuum-dried $RuCl_3/SiO_2$. This reduction temperature was observed to be 24°C lower than that obtained for the pure precursor. For the $RuCl_3/SiO_2$ which had been dried in air at 150°C the reduction temperature was observed to be 149°C, or 38°C lower than that of the unsupported $RuCl_3$. The measured enthalpy of reduction of the vacuum-dried $RuCl_3/SiO_2$ was determind by an ex-

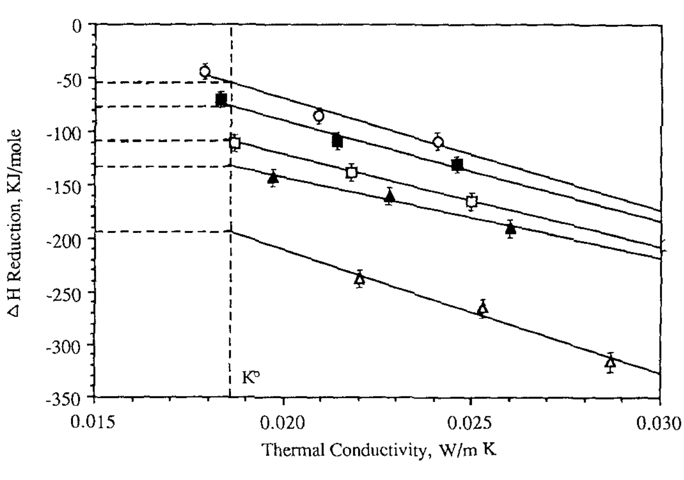

FIG. 2. The effect of purge gas thermal conductivity on the enthalpy of reduction of $RuCl_3$. (○) 0.5% H_2, (■) 1.0% H_2, (□) 1.5% H_2, (▲) 2.5% H_2, (△) 5% H_2.

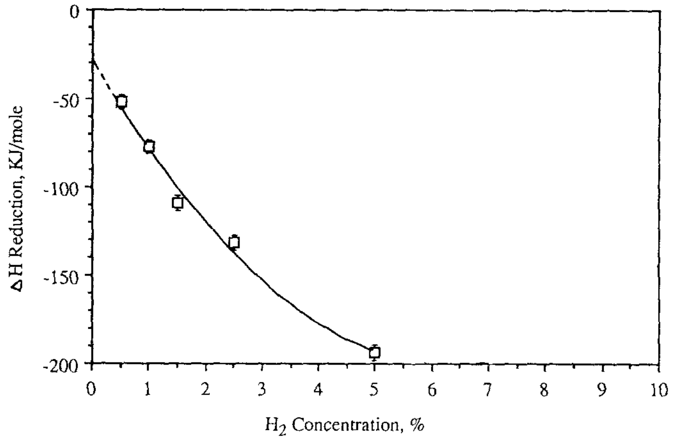

FIG. 3. The combined effect of purge gas thermal conductivity and H_2 concentration on the enthalpy of reduction of $RuCl_3$.

trapolation technique which was identical to that used for the pure precursor. The corresponding extrapolations for the vacuum-dried $RuCl_3/SiO_2$ are shown in Figs. 5 and 6. The enthalpies of reduction obtained by this method were observed to be −13 ± 1 kJ/mole for the vacuum-dried $RuCl_3/SiO_2$ and −3 ± 1 kJ/mole for the air-dried $RuCl_3/SiO_2$. A summary of these results, corrected for the small temperature dependence of the heat capacity, is shown in Table 1. Representative DSC scans for the unsupported and supported $RuCl_3$ are shown in Fig. 7.

Unsupported H_2PtCl_6. Unlike the reduction of $RuCl_3$, H_2PtCl_6 is reduced by a stepwise mechanism. A representative DSC profile of this reduction is shown in Fig. 8a. Using a H_2–Ar–He purge gas stream, the reduction of $H_2PtCl_6 \cdot 5H_2O$ was observed to be complete at 140°C. The five waters of hydration, in contrast to the normally reported six molecules of H_2O for H_2PtCl_6, were determined experimentally by gravimetric analysis. This value agrees well with the manufacturer's reported Pt content (38.84% Pt). Endotherms were observed at 76 and 95°C. Three exotherms centered at 101, 105, and 134°C were observed. These

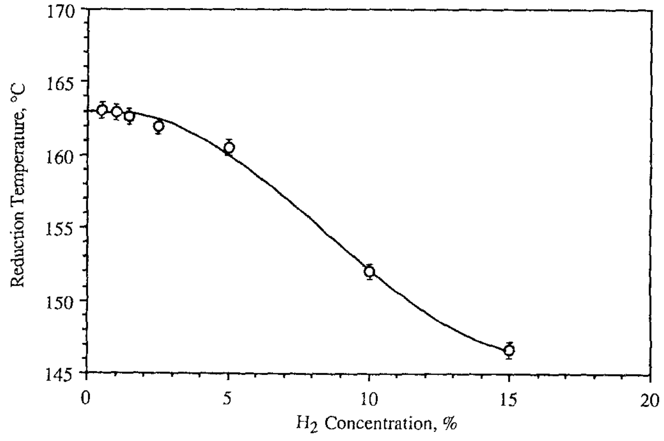

FIG. 4. The effect of H_2 concentration on the reduction temperature of vacuum-dried $RuCl_3/SiO_2$.

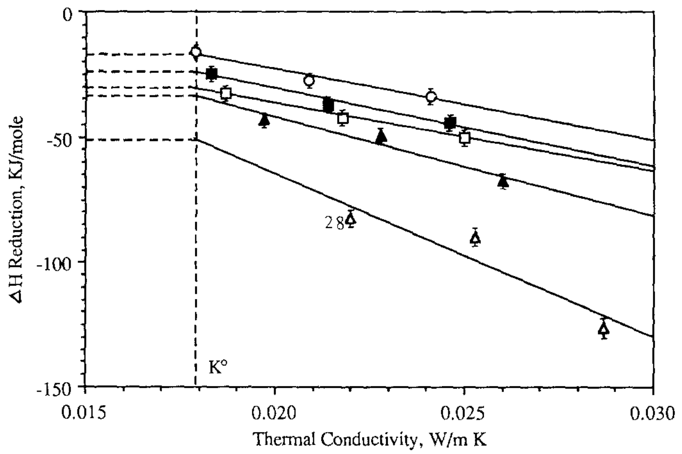

FIG. 5. The effect of purge gas thermal conductivity on the enthalpy of reduction of vacuum-dried $RuCl_3/SiO_2$. (○) 0.5% H_2, (■) 1.0% H_2, (□) 1.5% H_2, (▲) 2.5% H_2, (△) 5% H_2.

temperatures were determined by extrapolating the transition temperatures to zero H_2 concentrations. The temperatures corresponding to the two endotherms were not significantly affected by the concentration of H_2. However, the exotherms did show a significant dependence on H_2 concentration.

The occurrence of multiple endotherms and exotherms, which were unfortunately also convoluted, invalidated the use of the extrapolation technique used for the quantitative determination of the various enthalpies of decomposition and reduction as in the case of $RuCl_3$. In addition to peak convolution, the formation of mixed boundary layers of unknown composition consisting of H_2O and HCl made it exceedingly difficult to determine enthalpies for the individual steps in the reduction mechanism accurately. The total weight change ratio $\Delta W/W_0$ following reduction ($\Delta W/W_0 = 0.586 \pm 0.012$) closely corresponds to complete reduction to the metallic zero valent state ($\Delta W/W_0 = 0.612$) as shown by

$$H_2PtCl_6 \cdot 5H_2O + 3H_2 \rightarrow Pt + 6HCl + 5H_2O. \quad (2)$$

Experiments performed under He or N_2

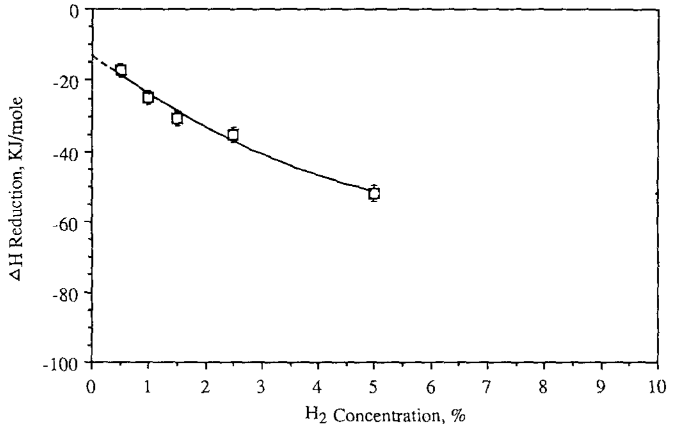

FIG. 6. The combined effect of purge gas thermal conductivity and H_2 concentration on the enthalpy of reduction of $RuCl_3/SiO_2$.

TABLE 1

Enthalpies (kJ/mole) and Temperatures (°C) of Reduction of RuCl$_3$

	Pure precursor (literature)[a]	Pure precursor (experimental)	Supported (vacuum-dried)	Supported (air-dried)
ΔH	-23.0	-29 ± 2	-13 ± 1	-3 ± 1
T_r	—	187	163 ±	149

[a] M. Kh. Karapetyants and M. L. Karapetyants, "Thermodynamic Constants of Inorganic and Organic Compounds," pp. 213–214. Ann Arbor Science Publishers, Ann Arbor, MI, 1970.

show that reduction (decomposition) is complete at a much higher temperature (about 450°C). Four decomposition endotherms centered at 75, 150, 190, and 426°C were observed. The overall change in weight ($\Delta W/W_0$) indicates complete decomposition to the zero-valent metallic state.

Supported H_2PtCl_6. The reduction of the supported vacuum-dried H$_2$PtCl$_6$/SiO$_2$ catalyst had only two thermal features: an endotherm centered at 72°C and an exotherm centered at 185°C. Both temperatures were obtained by extrapolation to zero H$_2$ concentration (Fig. 9). A representative DSC

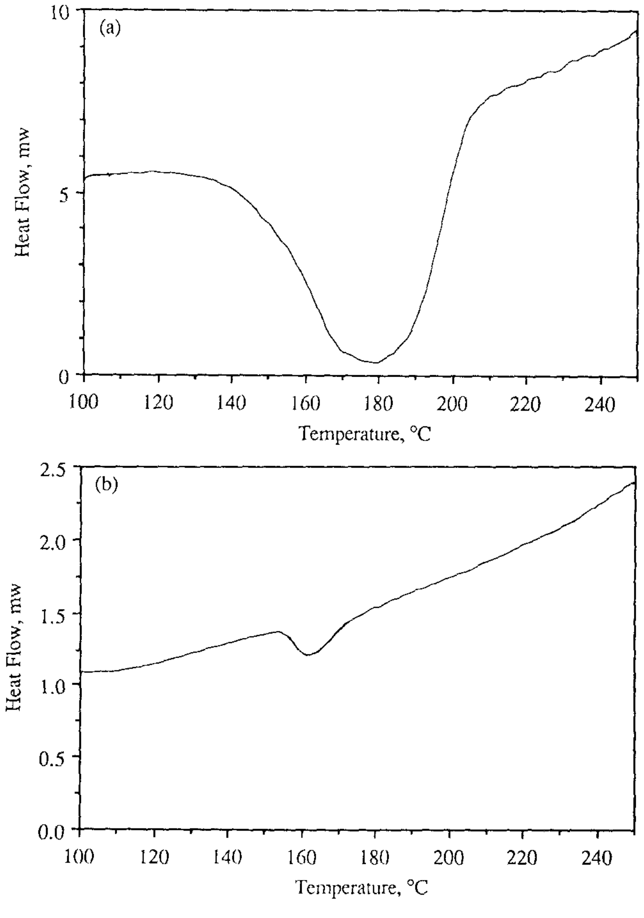

FIG. 7. Representative DSC profiles of reduction at 5% H$_2$ concentration; (a) RuCl$_3$, (b) RuCl$_3$/SiO$_2$.

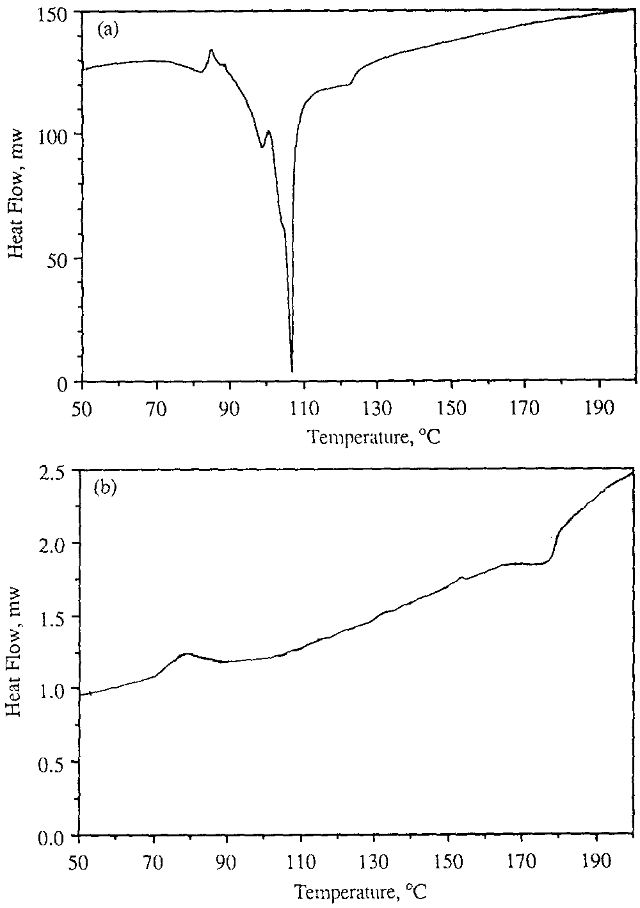

FIG. 8. Representative DSC profiles of reduction at 5% H_2 concentration; (a) H_2PtCl_6, (b) H_2PtCl_6/SiO_2.

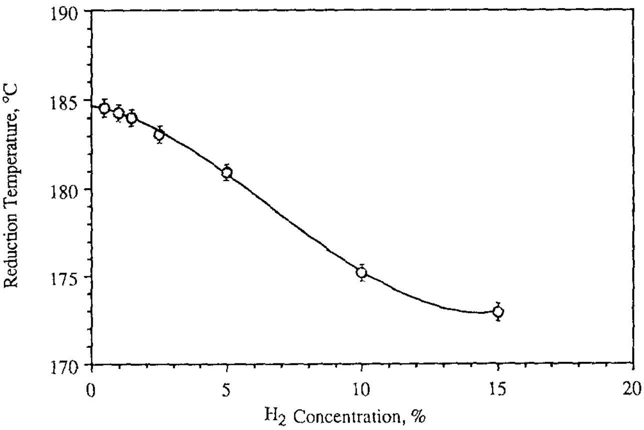

FIG. 9. The effect of H_2 concentration on the reduction temperature of vacuum-dried H_2PtCl_6/SiO_2.

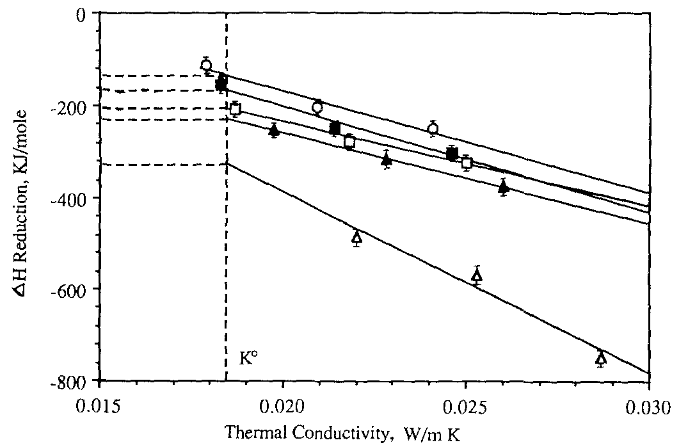

FIG. 10. The effect of purge gas thermal conductivity on the enthalpy of reduction of vacuum-dried H_2PtCl_6/SiO_2. (○) 0.5% H_2, (■) 1.0% H_2, (□) 1.5% H_2, (▲) 2.5% H_2, (△) 5% H_2.

profile for the supported H_2PtCl_6 is given in Fig. 8b. It is important to note that in contrast to $RuCl_3$, supported H_2PtCl_6 is reduced at a temperature which is considerably higher than that of its pure precursor (unsupported H_2PtCl_6). The enthalpy of reduction corresponding to the exothermic feature was determined by the double extrapolation technique to the thermal conductivity of the boundary layer (HCl) and zero H_2 concentration. These extrapolations are given in Figs. 10 and 11. The enthalpy of reduction obtained by this method was −115 ± 6 kJ/mole and was in reasonable agreement with the literature value (−122.6 kJ/mole) for the enthalpy of reduction of $PtCl_4$ based on standard heats of formation (*2*). Because of this result, we suggest that the endothermic feature centered at 72°C is due to the decomposition of supported H_2PtCl_6 to $PtCl_4$ with loss of two HCl molecules. The extrapolated enthalpy of the endothermic peak was 70 ± 2 kJ/mole.

For the series of catalysts dried in air at 150°C, the DSC profile showed thermal features which were similar to those obtained

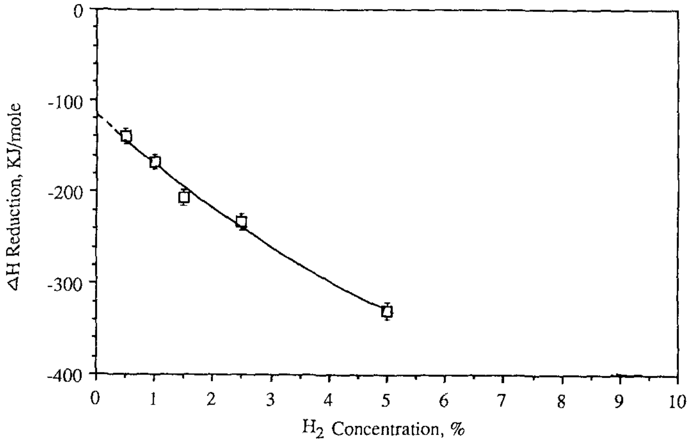

FIG. 11. The combined effect of purge gas thermal conductivity and H_2 concentration on the enthalpy of reduction of H_2PtCl_6/SiO_2.

TABLE 2

Enthalpies (kJ/mole) and Temperatures (°C) of Reduction of H_2PtCl_6

	Pure precursor (literature)[a]	Pure precursor (experimental)	Supported (vacuum-dried)	Supported (air-dried)
ΔH, end.	−251.0	140	70 ± 2	4 ± 1
ΔH, ex.	−122.6[b]	—	−115 ± 6	−107 ± 6
T_r, end.	—	95	72	60
T_r, ex.	—	134	185	189

[a] R. C. Weast and M. J. Astle, "CRC Handbook of Chemistry and Physics," pp. D67–D77. CRC Press, Boca Raton, FL, 1979.

[b] Due to the reduction of $PtCl_4$.

for the vacuum-dried catalysts. A small endotherm at a final extrapolated temperature of 60°C and an exotherm at 189°C were observed. An extrapolated enthalpy of −107 ± 6 kJ/mole was obtained for the exothermic peak, again suggesting the reduction of $PtCl_4$. The enthalpy of the endothermic peak was observed to be very small. Its extrapolated value of 4 ± 1 kJ/mole suggests a nearly complete decomposition of supported H_2PtCl_6 to $PtCl_4$ during exposure to air at 150°C. A summary of the results for H_2PtCl_6 is given in Table 2.

In order to further verify these observations, both the vacuum- and air-dried catalysts were examined by energy dispersive X-ray spectroscopy (EDXS) for elemental analysis. The results of this study are shown in Fig. 12. These experiments show a Cl/Si ratio of 0.233 for the vacuum-dried catalyst and 0.157 for the air-dried catalyst. The ratio of the amount of chlorine in the two catalysts is calculated as 0.673, in striking agreement with the calculated ratio for $PtCl_4$ and H_2PtCl_6 (0.67). The Pt/Si ratio was also determined by EDXS to be 0.512 for the vacuum-dried catalyst and 0.466 for the air-dried catalyst. Within the experimental reliability of EDXS, this agreement is satisfactory. It suggests that the Pt loading is independent of catalyst pretreatment.

Supported bimetallic catalysts. The reduction of both sets of bimetallics revealed only one exotherm rather than two separate peaks for Pt and Ru. The temperatures of reduction were obtained by extrapolation to zero H_2 concentrations. This extrapolation is shown for the 50% bimetallic catalyst which was vacuum dried (Fig. 13). The enthalpies of reduction were determined by the double extrapolation technique (Figs. 14 and 15) in a manner which was analogous to the procedure used for the monometallic catalysts. The final results for both sets of bimetallic catalysts are shown in Table 3. The observation of a single reduction exotherm suggests an assisted coreduction mechanism as a result of contact between the two metals. In order to verify this, a physical mixture of Pt/SiO_2 and Ru/SiO_2 catalysts was prepared and reduced under DSC. As expected, two separate peaks corresponding to the reduction of Pt and Ru were observed. This reduction profile is shown in Fig. 16. In order to observe the difference between the bimetallics and the physical mixture more clearly, the temperatures of reduction in addition to the enthalpies for the two series of Pt–Ru/SiO_2 bimetallic catalysts as determined by DSC are shown in Figs. 17 and 18, respectively. The temperatures and enthalpies of the physical mixture are calculated as the mole fraction average of the two monometallics and are shown by straight lines on both graphs. It can be observed that the enthalpies of the bimetallic catalysts are lower (more exothermic) than those which correspond to the physical mixture.

In order to determine the extent of interaction between the two metals, the initial precursor states of Pt and Ru were assumed

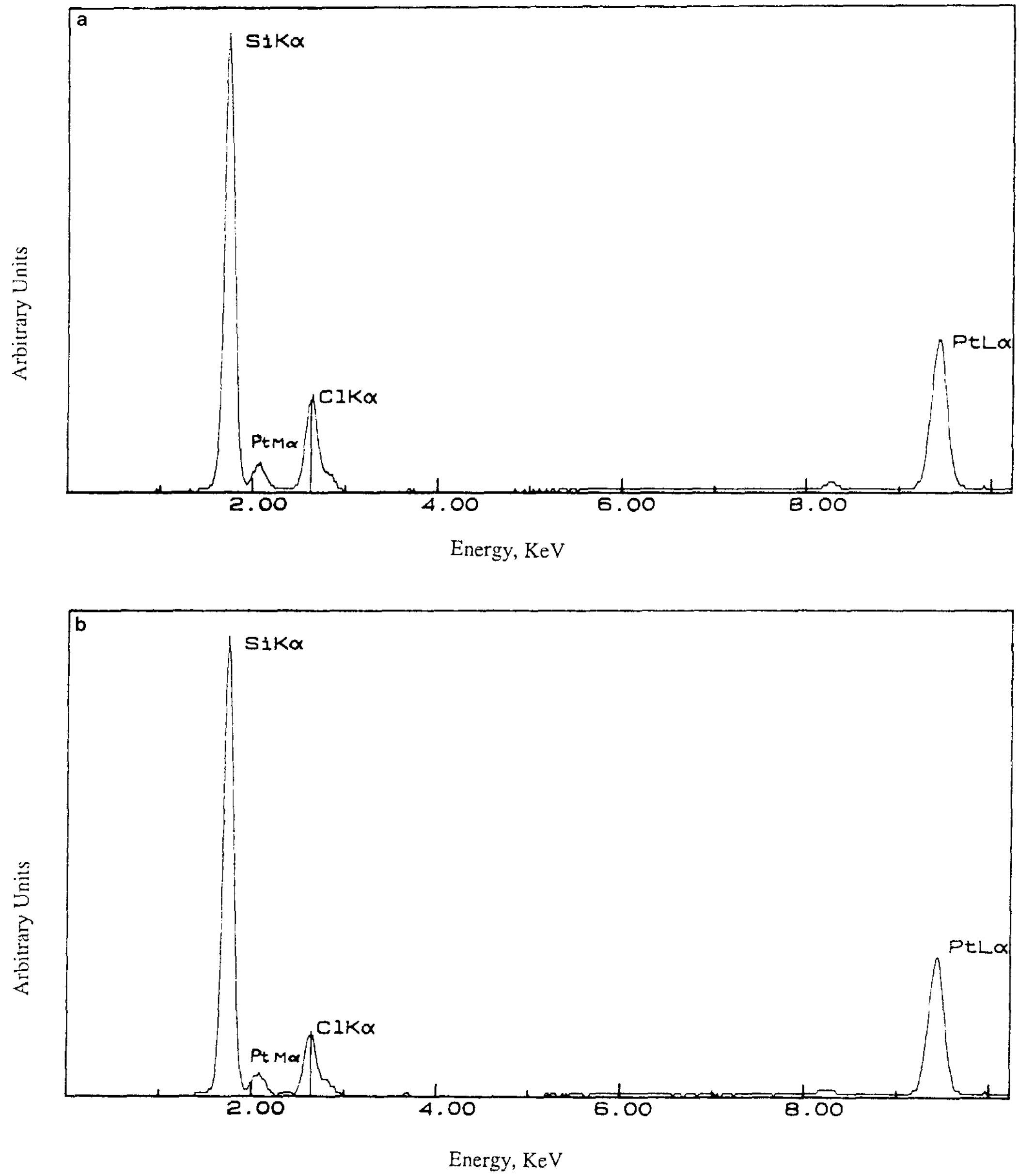

FIG. 12. The EDXS spectrum of H_2PtCl_6/SiO_2 catalysts, (a) vacuum-dried (b) air-dried.

to be $P1(PtCl_4)$ and $P2(RuCl_3)$ for both the physical mixtures and the bimetallics. These precursors were reduced to the separate metallic states M_1 and M_2 for the case of the physical mixture and to M_{12} for the bimetallic catalysts. The following thermodynamic equations for the reduction of the physical mixture as well as the bimetallic catalysts can be expressed as

Physical Mixture: $P_1 + P_2 \rightarrow M_1 + M_2$

$$\Delta H_r = -x_1 \cdot H_{p1} - x_2 \cdot H_{p2}$$

Bimetallic Cluster: $P_1 + P_2 \rightarrow M_{12}$

$$\Delta H_r = \Delta H_c - x_1 \cdot H_{p1} - x_2 \cdot H_{p2},$$

where x_1 and x_2 are mole fractions of Pt and Ru and ΔH_c is the heat of clustering. The heat of clustering can therefore be calcu-

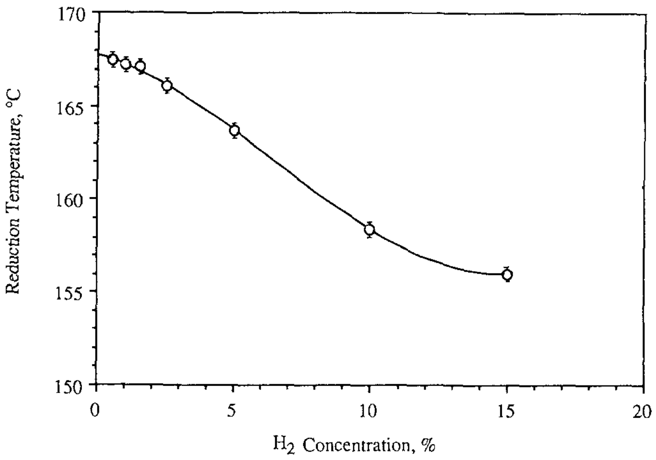

FIG. 13. The effect of H_2 concentration on the reduction temperature of the vacuum-dried 50–50 bimetallic catalyst.

lated from the enthalpy of reduction corresponding to the different metal compositions. These results are shown in Table 4 and Fig. 19.

It can be observed that in both sets of catalysts, the two metals cluster exothermically. For the air-dried catalysts, however, a slightly less exothermic effect is shown.

DISCUSSION

The temperature of reduction of the vacuum-dried Ru catalyst is comparable to that reported by Newkirk and McKee (*22*). These authors report a reduction temperature of approximately 160°C for both the supported and unsupported $RuCl_3$ using TGA. The results of this study show that when $RuCl_3$ is supported on silica, the reduction temperature, T_r, is decreased by 24°C for the vacuum-dried sample and by 38°C for the air-dried Ru catalysts. The magnitude of the enthalpy of reduction is reduced by a factor of 2 for the vacuum-dried catalyst (from −29 kJ/mole to −13 kJ/

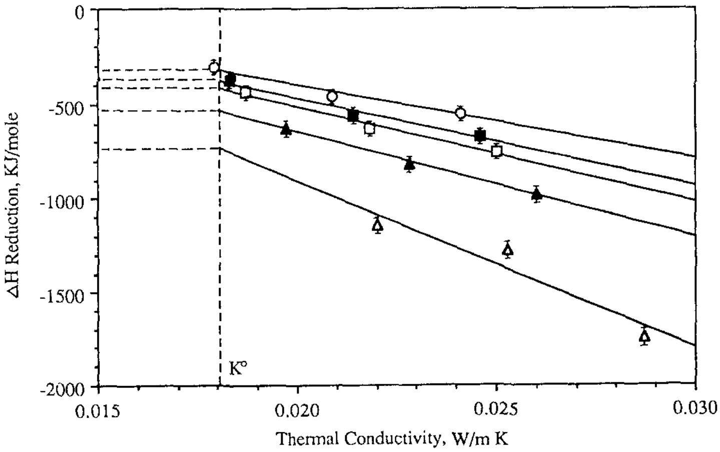

FIG. 14. The effect of purge gas thermal conductivity on the enthalpy of reduction of the vacuum-dried 50–50 bimetallic catalyst. (○) 0.5% H_2, (■) 1.0% H_2, (□) 1.5% H_2, (▲) 2.5% H_2, (△) 5% H_2.

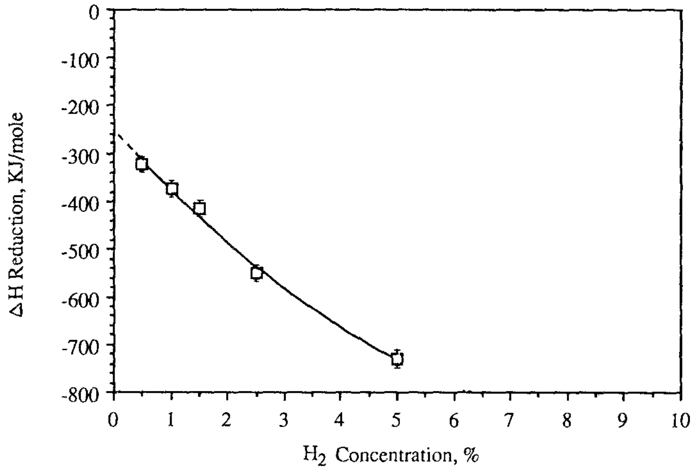

FIG. 15. The combined effect of purge gas thermal conductivity and H_2 concentration on the enthalpy of reduction of the vacuum-dried 50–50 bimetallic catalyst.

mole). In view of the complex structure of commercial $RuCl_3 \cdot 3H_2O$ (*24*), various cationic and anionic species such as $[RuCl(H_2O)_5]^{2+}$. $[RuCl_2)H_2O)_4]^+$, $[RuCl_4(H_2O_2]^-$, $[RuCl_5(H_2O)]^{2-}$, and $[RuCl_6]^{3-}$, in addition to possible Ru precursors for which the oxidation state of Ru may be a mixture of +3 or +4, may be present in the impregnating solution (*25*). Because the catalysts were prepared under acidic conditions at a pH which is higher than that corresponding to the isoelectric point of silica, these cations are readily exchanged with protons on the silica surface. This exchange results in the formation of a series of anchored ionic species with a poorly defined surface structure. This may be a reason for the decrease in reduction temperature. Air-dried Ru catalysts are reduced at a temperature which is 14°C lower than the vacuum-dried samples (149°C as opposed to 163°C). Additionally, the experimental enthalpy of reduction, ΔH_r, is reduced from -13 to -3 kJ/mole upon drying in air. Gravimetric results show that the anchored Ru species which had been dried in air lost more Cl than those which had been vacuum dried. Apparently the loss of chlorine results in a partial reduction of Ru which, in turn, leads to a substantial decrease in the temperature of reduction.

The gravimetric results obtained for hydrated H_2PtCl_6 suggest that there are approximately five waters of hydration per H_2PtCl_6 molecule. This was confirmed by the percentage Pt in the precursor (38.84%) reported by the manufacturer. The reduction of H_2PtCl_6 has been studied by several

TABLE 3

Temperatures (°C) and Enthalpies (kJ/mole) of Reduction for Supported Bimetallic Catalysts

% Pt	0	25	50	75	100
T_r, vacuum-dried	162.6	160.8	167.9	175.1	184.7
ΔH, vacuum-dried	−13	−154	−256	−197	−115
T_r, air-dried	149.0	153.0	160.1	169.4	186.5
ΔH, air-dried	−3	−88	−148	−136	−107

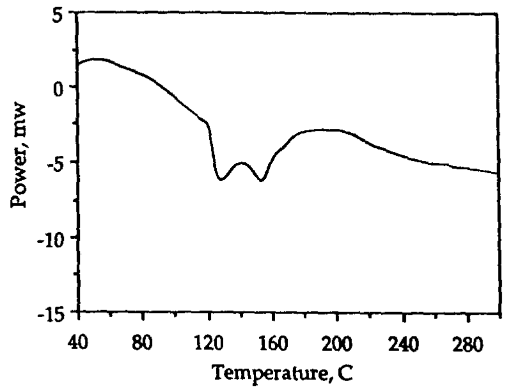

FIG. 16. The DSC profile of the reduction of a 25/75 physical mixture of Pt/SiO_2 and Ru/SiO_2 catalysts at 5% H_2 concentration.

research groups (*17*, *18*, *20*). Using temperature-programmed bulk reduction (TPBR), Hoyle *et al.* (*20*) observed two exotherms at 97 and 112°C. These were designated α and β and were observed to be highly convoluted. Schweizer and Kerr (*17*) reported that the reduction of H_2PtCl_6 by H_2 was complete below 100°C. Hernandez and Choren (*18*) observed only one endothermic reduction peak under H_2 flow. Several of the transformations reported in the literature involve restricted temperature ranges, i.e., 50–100 or 200–300°C. For this reason these studies may reflect the inaccuracy or insensitivity of the procedures used.

The fact that H_2PtCl_6 is reducible under He or N_2 has also been observed by other investigators (*17*, *18*). It has been reported that H_2PtCl_6 melts at 60°C and decomposes at 115°C (*26*). However, heats of fusion have not been reported. Our findings are in good agreement with these results. The enthalpy of fusion of H_2PtCl_6 found in this study was 19.0 kJ/mole.

Several conclusions can be drawn from the enthalpies and the temperatures of reduction of the supported Pt/SiO_2 catalysts (Table 2): (1) The relatively large number of endotherms and exotherms which were observed for the pure Pt precursor (H_2PtCl_6) merge into a doublet consisting of a single endotherm and an exotherm. (2) Unlike $RuCl_3/SiO_2$, the temperature of reduction which corresponds to the exotherm was substantially increased while that of the endotherm was decreased. (3) The enthalpies of reduction which correspond to the endotherm show a marked decrease in the sequence: Literature value > pure precursor > vacuum-dried > air-dried. The enthalpies of reduction which correspond to the exotherm, on the other hand, are remarkably constant and correspond to the enthalpy of reduction of pure $PtCl_4$.

From these observations we conclude that for the supported Pt catalysts, the precursor $[PtCl_6]^{2-}$ is partially decomposed

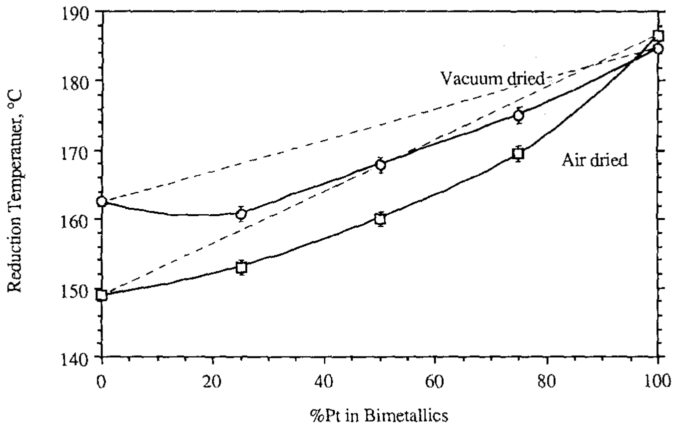

FIG. 17. The reduction temperatures of $Pt–Ru/SiO_2$ bimetallic catalysts.

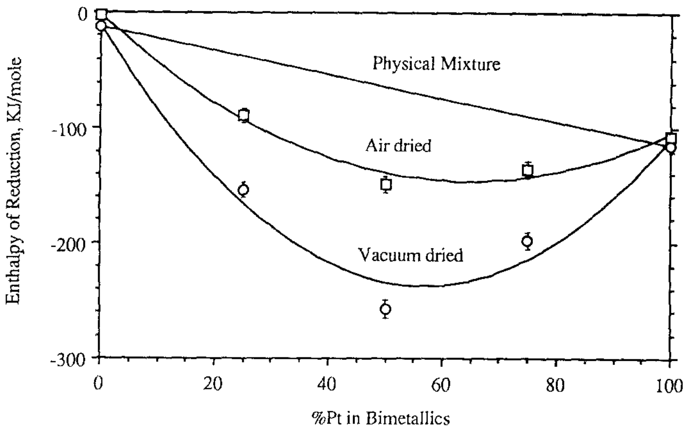

FIG. 18. The enthalpies of reduction of Pt–Ru/SiO$_2$ bimetallic catalysts.

into $PtCl_4$ as the result of vacuum drying and nearly totally decomposed to $PtCl_4$ as a result of air drying at 150°C. This result is apparent from the decrease in the enthalpy of the decomposition endotherm for the supported catalysts. Because the exotherms obtained for the supported catalysts are essentially equal to that of pure $PtCl_4$, there is little doubt that the observed exotherm corresponds to the reduction of supported $PtCl_4$, which interacts weakly with the support. The elemental analysis of chlorine obtained by EDXS (Fig. 12) is in excellent agreement with this interpretation.

The heat of clustering obtained for the supported bimetallic catalysts shown in Fig. 16 shows that the catalysts which were vacuum dried form bimetallic clusters by a strongly exothermic process. The catalysts which had been dried in air at 150°C showed a lower heat of clustering with respect to the mechanical mixture. This suggests that pretreatment in air may lead to a partial segregation of the Pt and Ru phases. This conclusion has been verified through the use of EDXS in which the elemental composition of a large number of particles was obtained. The results of this study, which will appear elsewhere (*27*), show that for the catalysts which had been vacuum dried, virtually all of the particles contained both Pt and Ru. A comparison of the ΔH_c data corresponding to the air-dried and vacuum-dried bimetallic catalyst shows that there appears to be a coreduction assistance process for both sets of bimetallic catalysts. Similar results were obtained by Bond *et al.* (*10, 12*) for the reduction of supported Ru–Cu catalysts. These authors found that treatment in oxygen followed by reduction in H_2 resulted in a single exotherm. These authors explained their results by invoking H_2 spillover. Even though H_2 is activated on Ru, the resultant chemisorbed hydrogen atoms can spill over from the Ru to the Cu provided that the particles are in reasonably close proximity

TABLE 4

Heat of Clustering (kJ/mole) at Various Compositions

% Pt	0	25	50	75	100
ΔH_c, vacuum-dried	0	−115.5	−192.0	−107.5	0
ΔH_c, air-dried	0	−59.0	−93.0	−55.0	0

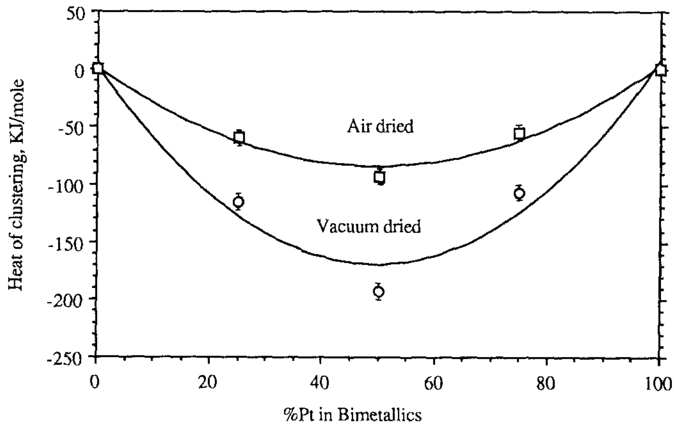

FIG. 19. The heat of clustering of Pt–Ru/SiO_2 bimetallic catalysts.

to one another. Perhaps a mechanism similar to that observed by Bond and Xu (*12*) is operative in the case of the air-dried Pt–Ru bimetallic clusters. However, the results for the mechanical mixture shown in Fig. 16 clearly show that when the Pt and Ru phases are separated, separate reduction exotherms are observed.

CONCLUSIONS

The following important conclusions emerge from this study:

(1) A precursor–support interaction is observed for silica-supported $RuCl_3$. A decrease in the temperature and enthalpy of reduction for supported $RuCl_3$ compared to that observed for the pure $RuCl_3$ precursor is suggestive of complex surface speciation of Ru.

(2) The measurement of the enthalpies of reduction of supported $PtCl_6^{2-}$ suggests that decomposition to $PtCl_4$ occurs at low temperatures. This decomposition to $PtCl_4$ is enhanced by drying in air at 150°C. The resultant $PtCl_4$ interacts weakly with the silica support.

(3) An exothermic bimetallic assisted coreduction process was observed for the supported Pt–Ru clusters. This exothermic interaction has a lower magnitude for the air-dried bimetallic samples. From these results we conclude that air drying results in partial separation of the Pt and Ru phases.

ACKNOWLEDGMENTS

The authors acknowledge support from the U.S. Department of Energy (Grant DOEFG02-86ER1351) and Amoco Corp. for this research.

REFERENCES

1. Rejai, B., and Gonzalez, R. D., *J. Catal.* **123,** 98 (1990).
2. Karapetyants, M. Kh., and Karapetyants, M. L., "Thermodynamic Constants of Inorganic and Organic Compounds," p. 213. Ann Arbor Science Publishers, Ann Arbor, MI, 1970.
3. Wiliams, F. L., and Nason, D., *Surf. Sci.* **45,** 377 (1974).
4. Miura, H., Suzuki, T., Ushikubo, K., Sugiyama, T., Matsuda, T., and Gonzalez, R. D., *J. Catal.* **85,** 331 (1984).
5. Miura, H., Feng, S. S., Saymeh, R., and Gonzalez, R. D., *ACS Symp. Ser.* **288**(25), 294 (1985).
6. Gonzalez, R. D., *Appl. Surg. Sci.* **19,** 181 (1984).
7. Augustine, S. M., Sachtler, W. M. H., Butt, J. B., Nacheff, M. S., and Tsang, C. M., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1190. Chem. Institute of Canada, Ottawa, 1988.
8. Miura, H., personal communication.
9. Galvano, S., Crisafulli, C., Maggiore, R., Giannetto, A., and Schwank, J., *J. Therm. Anal.* **32,** 471 (1987).
10. Bond, G. C., and Turnham, D., *J. Catal.* **45,** 128 (1976).

11. Damiani, D. E., Perez Millan, E. D., and Rouco, A. J., *J. Catal.* **101,** 162 (1986).

12. Bond, G. C., and Xu, Y., *J. Molec. Catal.* **25,** 141 (1984).

13. Hong, A. J., McHugh, B. J., Bonneviot, L., Resasco, D. E., Weber, R. S., and Haller, G. L., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1198. Chem. Institute of Canada, Ottawa, 1988.

14. Anderson, J. R., "Structure of Metallic Catalysts," pp. 164–197. Academic Press, New York, 1975.

15. Diaz, G., Garin, F., and Maire, G., *J. Catal.* **82,** 13 (1983).

16. Alerasool, S., Boecker, D., Rejai, B., Gonzalez, R. D., del Angel, G., Azomosa, M., and Gomez, R., *Langmuir* **4**(5), 1083 (1988).

17. Schweizer, A. E., and Kerr, G. T., *Inorg. Chem.* **17**(8), 2326 (1978).

18. Hernandez, J. O., and Choren, E. A., *Thermochim. Acta* **71**(3), 265 (1983).

19. Kinoshita, K., Routsis, K., and Bett, J. A. S., *Thermochim. Acta* **10,** 109 (1974).

20. Hoyle, N. D., Newbatt, P. H., Rollins, K., Sermon, P. A., and Wurie, A. T., *J. Chem. Soc. Faraday Trans. 1* **81,** 2605 (1985).

21. Jenkins, J. W., McNicol, B. D., and Robertson, S. D., *Chem. Tech (Leipzig)*, 316 (1977).

22. Newkirk, A. E., and McKee, D. W. *J. Catal.* **11,** 370 (1968).

23. Wassiljewa, A., *Phys. Z.* **5,** 737 (1904).

24. Gouzerh, P., Jeannin, Y., Rocchiccioli-Deltcheff, C., and Valentini, F., *J. Coord. Chem.* **6,** 221 (1979).

25. Griffith, W. P., "The Chemistry of the Rarer Platinum Metals." Interscience, London, 1967.

26. Weast, R. C., and Astle, M. J., "CRC Handbook of Chemistry and Physics," pp. D67–D77. CRC Press, Boca Raton, FL, 1979.

27. Del Angel, G., Dominguez, J. M., Gomez, R., Gonzalez, R. D., and Alerasool, S., *Surface Science* **224,** 407 (1989).