JOURNAL OF CATALYSIS **111**, 59–66 (1988)

Analysis of Temperature-Programmed Reduction Profiles from Metal-Supported Catalysts

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Received August 20, 1987; revised December 1, 1987

An experimental procedure is proposed to enable analysis of H_2 emission/consumption data obtained during temperature-programmed reduction (TPR) of a metal-supported catalyst. Using the methods described allows one to account for chemical processes other than reduction and thus remove their contribution from the TPR profile. The resulting "real" TPR spectrum is a signature that reflects only reduction processes that occur under nonisothermal conditions. To demonstrate the methodology, Pt, Ir, and Pt/Ir supported on alumina have been characterized. The real TPR profile of the bimetallic catalyst is not the simple superposition of the reduction spectra of the monometallics. This observation has generally been considered indicative of some type of alloy-phase formation. On the other hand, had the hydrogen emission/consumption data been used directly, the same conclusion would be tenuous.

INTRODUCTION

Temperature-programmed reduction (TPR) is a recently developed technique used to chemically characterize supported metal catalysts (*1*, *2*). During TPR, a hydrogen-containing gas mixture continuously perfuses the catalyst bed while the temperature of the bed is raised linearly with time. By measuring the consumption of hydrogen as a function of temperature, a so-called TPR profile is obtained. The use of such profiles provides fingerprints of the chemical nature and environment of the catalytic component. Furthermore, the area under the TPR peak reflects the concentration of that component present on the catalyst surface. Due to its ease in use by providing quick assessment of the differences between catalysts prepared via different conditions, the practical applications of TPR have increased dramatically.

TPR has been applied to the characterization of catalysts or catalytic precursors at different stages of the catalyst preparation sequence. The sample can be either passivated (*3–5*) or unpassivated (*4*, *5*). The sample can also be bulk (*6–8*), supported monometallic (*4*, *5*, *8*, *9*), or supported bimetallic materials (*10*, *11*). The TPR technique is extremely sensitive to the pretreatment of the catalyst prior to experimentation. Different pretreatments result in different catalytic precursors; the TPR profile is a record of the reduction of these precursors. It is likely that the precursor pool will contain a variety of species, each with its own characteristic reduction profile. The resulting TPR spectrum is a composite of these processes with some contribution likely from processes that do not involve changes in the oxidation state of the metal.

During the TPR process, the oxidation states of the supported metal cations decrease, resulting in a hydrogen consumption. This reduction process ceases after all the reducible metal cations are consumed. *The reduced metal*, however, *is capable of adsorbing hydrogen from the gaseous environment*. At the same time, the adsorbed hydrogen can desorb into the flowing hydrogen-containing carrier gas. In some cases, the chemisorbed hydrogen may diffuse along the surface of the catalyst. This

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0021-9517/88 $3.00

spillover hydrogen can desorb from the support at higher temperature (*12*). Therefore, the apparent hydrogen consumption/emission is composed of additional chemical processes that *do not* involve changes in oxidation state.

The apparent hydrogen consumption/emission, based on the mass balance of these contributions, can be written as

$$\begin{aligned}&\text{apparent hydrogen consumption/emission}\\&\quad = \text{reduction} + \text{adsorption} + \text{spillover}\\&\quad - \text{desorption of chemisorbed hydrogen}\\&\qquad - \text{desorption of spillover hydrogen.}\end{aligned}$$

The adsorption/desorption process is an inherent property of the reduced metal and is unavoidable. The contribution from hydrogen spillover may be significant on some metals, such as platinum (*12*). Furthermore, the rates for these processes are temperature dependent and their contributions may obscure the reduction profile during the TPR process which is also a temperature-dependent process. The first term on the right-hand side of the above equation consists of two components: an isothermal contribution and a temperature-programmed component. The former occurs when the sample is exposed to the reducing gas mixture at the initial temperature of the experiment; the latter occurs during the temperature ramp and is typically designated the TPR profile.

In conjunction with the mass balance equation and the recognition of a possible isothermal reduction process, the "real" TPR profile can be obtained. We define the real TPR profile as that signature that reflects *only* reduction processes that occur during temperature programming.

The objective of this report is to demonstrate the use of a sequence of experiments to account for the isothermal reduction, the adsorption/desorption, and the spillover contributions during the TPR process and provide a basis for interpreting TPR results. The contributions from the aforementioned processes need to be determined to obtain the *real* TPR profile. This consideration becomes more important when TPR is used to study bimetallic catalysts where the characteristics of a TPR spectrum are used to obtain evidence of the interaction between the atoms of the two metallic components. We applied these procedures to obtain evidence for intimate contact between constituent metals in the $Pt/Ir/Al_2O_3$ system.

EXPERIMENTAL

Catalysts

Ir/Al_2O_3 (4.4%), Pt/Al_2O_3 (4.4%), and $Pt/Ir/Al_2O_3$ (4.5% Pt, 6.5% Ir) catalysts were used in this study. All catalysts were prepared by wet impregnation using H_2PtCl_6 and H_2IrCl_6 as impregnation reagents. Two grams of γ-alumina was brought into contact with 25 ml of the impregnation solution at a concentration sufficient to mount *0.3% by weight* of metals on the support based on pore filling. A particle size of 0.225 mm was used to ensure a uniform metal distribution throughout the support particles. The slurry was continuously agitated for 1 h, a time sufficient for adsorption equilibrium (*13*). The metal concentration in solution before and after contact with the support was determined with a Perkin–Elmer Model 2380 atomic adsorption spectrophotometer. All catalyst precursors were dried at room temperature, calcined at 120°C for 1 h, and finally calcined at 400°C for 4 h.

A large amount of adsorption of Ir and Pt to the alumina support is observed when the catalysts are prepared by wet impregnation. The pH's of the H_2IrCl_6 and H_2PtCl_6 solution, with a concentration necessary to mount 0.3% metal by weight, are 1.5 and 1.4, respectively. Dissociation of H_2IrCl_6 and H_2PtCl_6 yields anions in the aqueous phase. In this pH range, the γ-alumina (pH_{zpc} = 7.8) (*14*) possesses a positively charged surface. Thus, the amount of adsorption due to the attractive static force between a positively charged surface and the anions is expected to be strong, and results in a catalyst with high weight loading (4.4%).

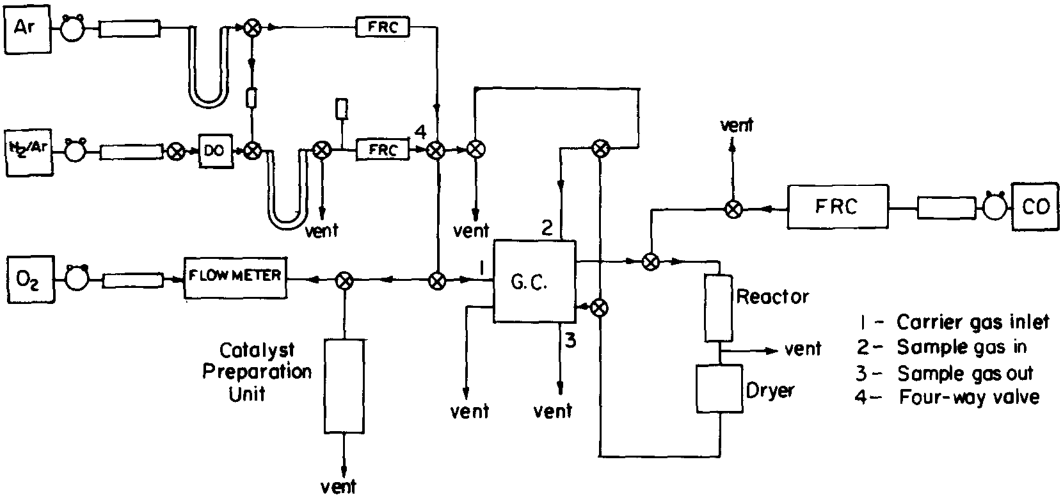

FIG. 1. Schematic diagram of the TPR apparatus. Note that the Ar on H_2/Ar stream can be directed into the reactor via the four-way valve, 4.

Apparatus

The TPR apparatus used in this study is schematically represented in Fig. 1. An 8.5% H_2 in Ar stream can be directed through a microreactor. The flow rates of gases are controlled with Tylan Controllers (Model FC-260); the temperature of the reactor is controlled with an Omega microprocessor temperature programmer. The temperature of the reactor can be programmed to increase linearly from room temperature to 500°C. The procedures described below are general and choice of starting temperature should be dictated by available experimental facilities. H_2 consumption is monitored continuously with an IBM PC-XT interfaced to a Fisher Model 1200 gas partitioner in which the built-in thermal conductivity detector (TCD) is used to monitor changes in H_2 concentration in the carrier stream.

Procedures

It is necessary to allow the TCD detector to stabilize in an 8.5% H_2/Ar flow before the temperature ramp is performed. Inevitably, some of the sample may be reduced during the isothermal stabilization period. This reduction behavior cannot be neglected and needs to be considered separately. Although methods have been proposed by Prins and co-workers (*4*), they are qualitative. We suggest below simple procedures to assess the hydrogen consumption during isothermal reduction. The experimental procedures are divided into two parts: the amount of hydrogen consumed during the isothermal reduction period (i.e., the period for TCD stabilization before the temperature is raised) is described in Part I and the amount of metal reduced during the temperature ramp period is described in Part II.

Part I: Experimental Sequence for TPR

1. Dehydration. Sample (100 mg) is flushed with Ar at a flow rate of 100 cm^3/min. The temperature is raised to 500°C at a heating rate of 5°C/min. The sample is held at 500°C for 1 h and cooled to room temperature in flowing Ar.

2. Reduction. The Ar stream is switched to 8.5% H_2/Ar at a flow rate of 40 cm^3/min. After the TCD is stabilized, a calibration procedure is performed to account for the difference in sensitivity from run to run. Some of the sample may be reduced during the TCD stabilization period. The amount of H_2 consumed during this period is determined in a separate experiment described in Part II. To calibrate, 0.1, 0.3, and 0.5 μl of Ar are injected into the TCD. After the TCD has been calibrated, the temperature of the reactor is raised to 500°C at a heating rate of 20°C/min and held at 500°C for 20 min. The apparent hydrogen consumption/emission data and the temperature of the catalyst bed are continuously recorded on the IBM PC-XT. The resulting spectrum is designated as the first TPR spectrum. The catalyst is flushed with an Ar gas flow at 500°C for 5 min and cooled to room temperature at a cooling rate of about 20°C/min.

3. Adsorption/desorption. The Ar gas flow is switched to the H_2/Ar gas stream and the procedures used in the reduction step are repeated. The resulting spectrum is designated the second TPR spectrum. After the second TPR spectrum had been recorded, the catalyst is cooled to room temperature in H_2/Ar instead of Ar. The resulting hydrogen consumption spectrum during cooling is designated as the adsorption spectrum.

It is interesting to note that the second TPR spectrum should be a mirror image of the adsorption spectrum for a completely reduced catalyst for which there is no contribution from hydrogen spillover. If the adsorption spectrum is not a mirror image of the second TPR spectrum, an additional TPR experiment is necessary to determine whether the catalyst is completely reduced or hydrogen spillover is dominating. Following the procedures described in Step 2, the resulting TPR spectrum is designated the third TPR spectrum. Similarity of the spectra of the second and third TPRs implies that the catalyst has been reduced during the first TPR process and the second TPR is obtained from a completely reduced surface, i.e., a temperature-programmed desorption (TPD) spectrum. Dissimilarity suggests that the catalyst is not fully reduced. For a catalyst with incompletely reduced metal, Steps 2 and 3 should be repeated until the two spectra are the same.

After the adsorption spectrum is recorded, a temperature-programmed desorption (TPD) experiment is suggested to obtain additional information regarding the H_2 binding strength on the supported metal(s). Although the results will not be presented in this report, the suggested TPD experiment is described as follows.

4. Temperature-programmed desorption. After the adsorption spectrum has been recorded, the gas stream is switched to Ar. The TCD is stabilized and calibrated and the temperature is increased linearly with time. The rate of hydrogen emission and catalyst temperature are recorded continuously to yield the TPD spectrum.

Part II: Experimental Sequence for Isothermal Reduction

1. Dehydration. An aliquot of 100 mg of the sample used in the previous TPR experiments is dehydrated in flowing Ar by the same procedure described in the Step 1 of Part I. The dehydrated sample is cooled to room temperature in flowing Ar.

2. Room-temperature reduction/adsorption. The Ar stream with a flow rate of 40 cm^3/min is then directed to the TCD via a four-way valve. After the TCD is stabilized, several pulses of 8.5% H_2/Ar are injected into the reactor by a built-in internal sampling loop with a volume of 0.25 cm^3 per pulse. The injection of H_2/Ar is repeated until the breakthrough of pulses occurs.

The reduced metal can adsorb hydrogen during room-temperature reduction. The amount of hydrogen adsorbed can be assessed by the following procedures.

3. Temperature-programmed desorption. The temperature is programmed to increase linearly from ambient to 500°C in Ar at a rate of 20°C/min. The flow rate of Ar is 40 cm^3/min. The resulting spectrum of hydrogen emission as a function of temperature is a TPD spectrum. After the TPD spectrum is recorded, the sample is cooled to room temperature in flowing Ar.

The amount of hydrogen adsorbed during TPD can be calculated by integrating the area under the TPD spectrum. However, the adsorbed hydrogen can react with the unreduced part of the sample. To assess this portion of the adsorbed hydrogen, an additional TPR experiment is necessary.

4. Temperature-programmed reduction. The Ar stream is switched to the 8.5% H_2/Ar stream. After the TCD is stabilized and calibrated, a temperature-programmed reduction experiment is performed on the sample by the same procedures described in Step 3 of Part I. The difference between the resulting TPR spectrum and the first TPR spectrum obtained in Part I is the amount of H_2 consumed during the previous TPD experiment. The sum of the H_2 consumption in Steps 3 and 4 is the total amount of H_2 adsorbed during room-temperature reduction. Subtraction of the amount of adsorbed H_2 (Steps 3 and 4) from the amount of H_2 consumed during room-temperature reduction (Step 2) yields the amount of H_2 consumed due to the reduction of the sample at room temperature.

RESULTS AND DISCUSSION

To demonstrate the procedures outlined in Part I of the previous section we present results of the temperature-programmed reduction of Ir, Pt, and Pt/Ir/Al_2O_3 catalysts.

Ir/Al_2O_3 Catalyst

Figure 2a shows the first TPR spectrum. It demonstrates that the apparent hydrogen consumption occurs when the temperature is lower than 200°C. However, an apparent hydrogen emission is detected in the temperature range 200 to 360°C. Figure 2a shows the combined contributions from reduction, adsorption, and desorption. It clearly indicates that one cannot separate the real reduction profile from the first TPR spectrum alone.

Figure 2b shows the second TPR spectrum; hydrogen emission is observed during the second TPR process. Figure 2c shows the adsorption spectrum when the catalyst is cooled in a H_2/Ar gas stream.

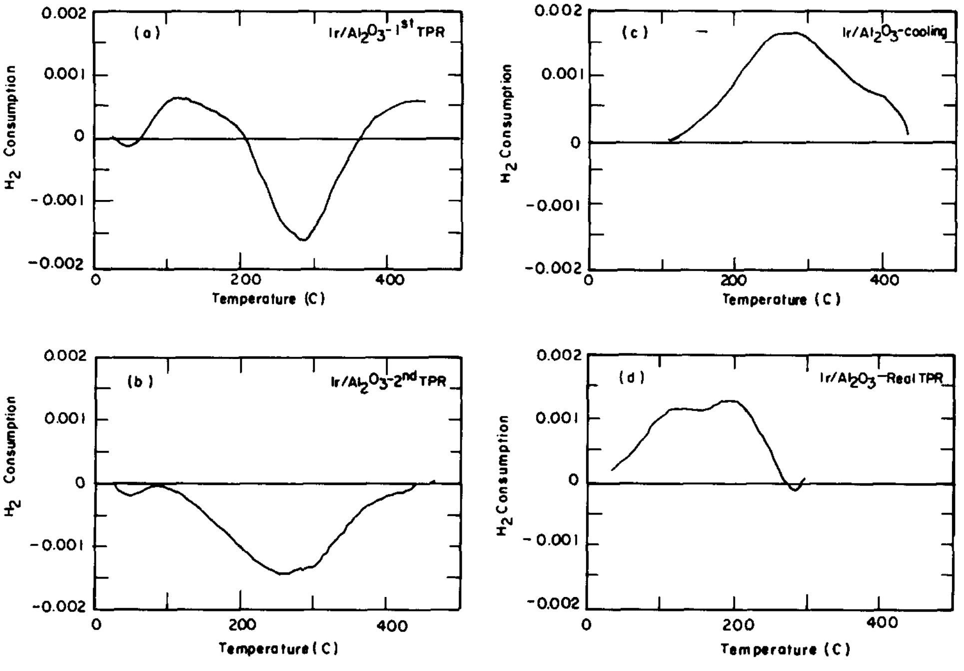

FIG. 2. (a) The first TPR spectrum, (b) the second TPR spectrum, (c) the cooling curve, and (d) the "real" TPR spectrum of a 4.4% Ir/Al_2O_3 catalyst.

TABLE 1

Hydrogen Consumption for Ir/Al_2O_3, Pt/Al_2O_3, and $Pt/Ir/Al_2O_3$ Catalysts during TPR Process

Catalyst	H_2 consumption (μmol/g catalyst)
4.4% Ir/Al_2O_3	100
4.4% Pt/Al_2O_3	110
4.5% Pt/6.5% Ir/Al_2O_3	180

Figure 2c is a mirror image of Fig. 2b. It implies that the catalyst surface is free of unreduced Ir before the second TPR is performed. It further demonstrates that the hydrogen spillover process is not significant in this case. In conjunction with the mass balance equation for the apparent hydrogen consumption/emission, it is important to note that *the second TPR spectrum is the combined contributions of adsorption and desorption during the TPR process.*

A real TPR profile can thus be obtained by subtracting Fig. 2b from 2a and the resulting TPR profile is Fig. 2d. It shows that two peaks are observed at 100 and 200°C. Table 1 tabulates the amount of H_2 consumed for this catalyst during the TPR process.

Pt/Al_2O_3 Catalyst

Figures 3a and b are the spectra of the first TPR and second TPRs, respectively. Hydrogen consumption is observed during the first TPR process, but hydrogen emission is observed during the second TPR process. An additional feature of the second TPR spectrum is that a long tail for hydrogen desorption is observed between 300 and 400°C. Figure 3c is the adsorption spectrum during cooling. Figure 3c is clearly not a mirror image of Fig. 3b. An additional TPR process is performed, and the resulting third TPR spectrum is Fig. 3d. Figure 3d is identical to Fig. 3b, implying that the catalyst surface is completely reduced during the first TPR experiment. The long tail for hydrogen desorption observed in the second TPR spectrum is tentatively assigned to the desorption of spillover hydrogen from the support. The temperature range observed for the desorption of spillover hydrogen is consistant with other investigators' results (*12*). The high hydrogen consumption observed in the adsorption spectrum is tentatively assigned to the combined processes of hydrogen chemisorption on the metal function and the repopulation of spillover hydrogen previously desorbed during Step 3. Therefore, the second TPR spectrum can be used to account for the hydrogen adsorption, desorption, and spillover during the first TPR experiment. Subtraction of Fig. 3b from 3a yields Fig. 3e, the real TPR spectrum. It has a singular peak at 210°C. The H_2 consumption of this catalyst during the TPR process is tabulated in Table 1.

$Pt/Ir/Al_2O_3$ Catalyst

Figure 4a is the first TPR spectrum for the $Pt/Ir/Al_2O_3$ bimetallic catalyst. It shows that an apparent hydrogen consumption occurs between 80 and 220°C. However, hydrogen emission is observed between 220 and 300°C. Figure 4b is the second TPR spectrum. It shows that an apparent H_2 emission is observed. Figure 4c is the adsorption spectrum of the catalyst cooled in H_2/Ar. The observation that Fig. 4c is a mirror image of Fig. 4b implies that Fig. 4b is obtained from a reduced surface. The subtraction of Fig. 4b from Fig. 4a yields the real TPR profile and the resulting spectrum is Fig. 4d. It shows a singular peak at 170°C. The H_2 consumption during the TPR process is tabulated in Table 1.

The peak temperature of the reduction of the Pt/Ir bimetallic catalyst (170°C) is neither the reduction peak temperature(s) of the individual monometallic catalysts (Ir: 100 and 200°C; Pt: 210°C) nor the peak temperature at the sum of the TPR spectra of the individual monometallic catalysts. Although the result of the summation of the TPR spectra (i.e., Figs. 2d and 3e) is not shown in this report, the TPR spectrum

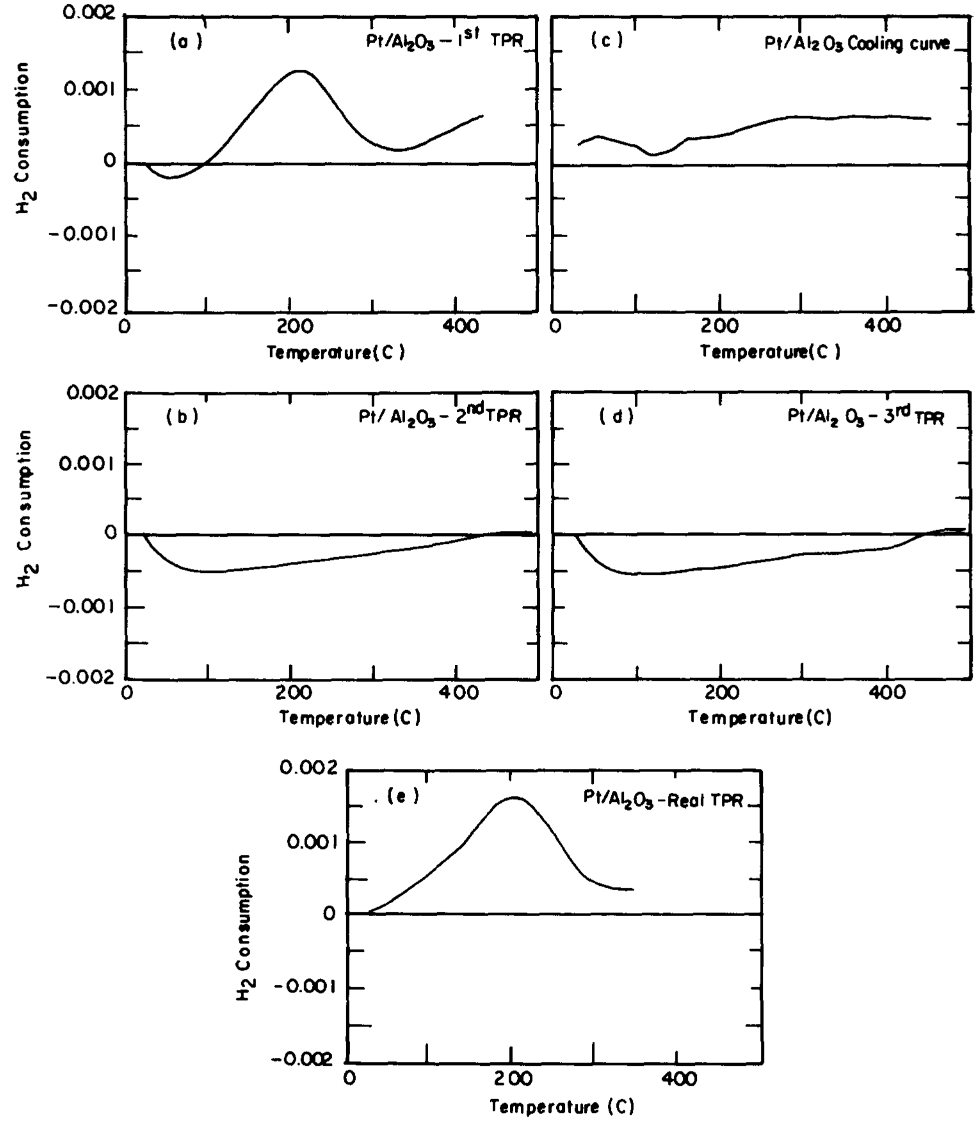

FIG. 3. (a) The first TPR spectrum, (b) the second TPR spectrum, (c) the cooling curve, (d) the third TPR spectrum, and (e) the "real" TPR spectrum of a 4.5% Pt/Al_2O_3 catalyst.

would show two peaks at about 100 and 200°C. Had only the hydrogen *consumption* portions of the first TPR for Ir (Fig. 2a) and Pt (Fig. 3a) been considered, their summation would be very similar to the hydrogen consumption of the bimetallic catalyst (Fig. 4a). Furthermore, the area under this portion of the curve is such that the total consumption of the monometallics is approximately the same as that of the bimetallic. Any conclusions concerning alloy/new phase formation in these catalysts would be tenuous had the first TPR spectra been analyzed.

On the other hand, the result shown in Fig. 4d, the real TPR spectrum, demonstrates that the presence of both Pt and Ir affects the reduction behavior of each considered separately. The results obtained using the TPR procedures outlined in this

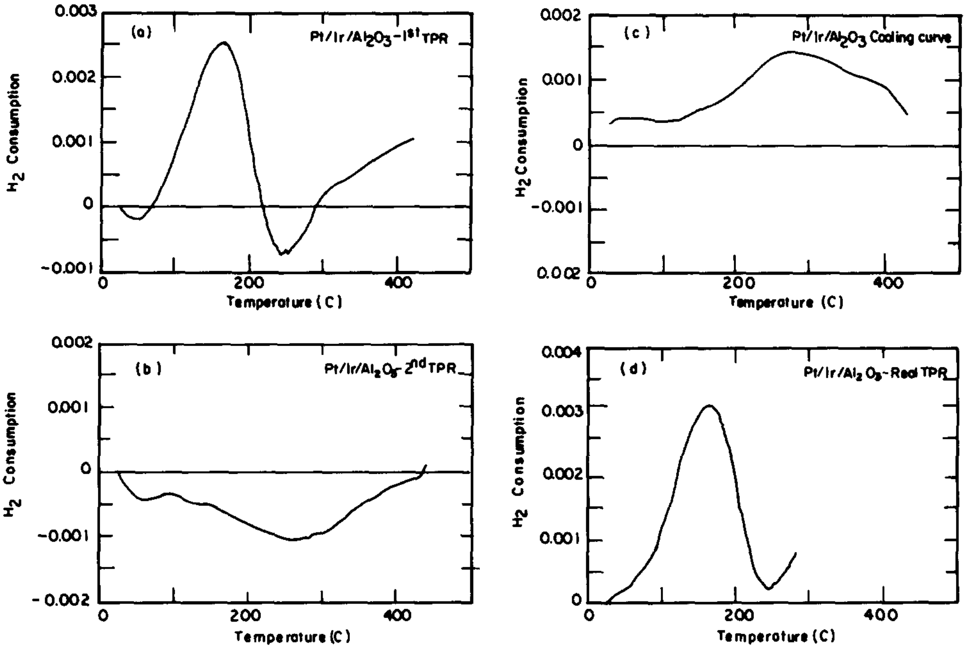

FIG. 4. (a) The first TPR spectrum, (b) the second TPR spectrum, (c) the cooling curve, and (d) the "real" TPR spectrum of a 4.5% Pt/6.5% Ir/Al_2O_3 catalyst.

study strongly suggest that a single-phase bimetallic cluster, rather than two separate monometallic phases, exists on the catalyst surface. Results obtained by other investigators using other techniques, such as EXAFS (*15*), XRD (*16*), and Mössbauer effect spectroscopy studies (*17*), have confirmed the hypothesis that an alloy-type bimetallic cluster does exist on the surface after the bimetallic catalyst has been reduced. The TPR technique, taking into account the contributions of adsorption and desorption via the procedures suggested above, can be used confidently to characterize the catalyst by probing its temperature-dependent *reduction* properties.

ACKNOWLEDGMENT

This work was partially supported by Exxon Research and Engineering Company.

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