

## The Hydrogenolysis of Ethane over Re–Pt(111) and Pt–Re(0001) Bimetallic Crystal Surfaces

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Platinum–rhenium bimetallic surfaces were prepared by condensing both rhenium on the (111) face of platinum, and platinum on the (0001) face of rhenium from the vapor under ultrahigh vacuum. Using a high-pressure microreactor, the hydrogenolysis of ethane was investigated over the small-area catalysts in the temperature range 300–350°C, with pressures of 5–10 Torr ethane and 100–1000 Torr hydrogen. The reaction is structure sensitive on both platinum and rhenium as indicated by the large increase in the initial rates of reaction observed after the Pt(111) and Re(0001) surfaces were roughened by argon ion bombardment. The Re(0001) surface was two orders of magnitude more active than the Pt(111) surface, yet a bimetallic surface of the stoichiometry Re<sub>2</sub>Pt was found to be the most active surface for ethane hydrogenolysis—about one order of magnitude more active than the Re(0001) surface. Thus the activity of the bimetallic catalyst is not a linear combination of the activities due to the two metallic components. Hydrogen pressure dependence studies show that a bimetallic surface composed of 0.3 monolayer of rhenium on Pt(111) had an activity close to that of a monometallic Re(0001) surface, yet displayed a hydrogen partial pressure dependence closer to that of a Pt(111) surface. These results suggest that an electronic interaction exists between platinum and rhenium metals that strongly influence the catalytic hydrogenolysis of ethane. The accumulation of carbonaceous deposits was fairly insensitive to temperature and hydrogen pressure on rhenium and bimetallic Pt–Re surfaces. However, the accumulation of carbonaceous deposits on monometallic Pt(111) surfaces was highly sensitive to the reaction conditions, and adsorbed on this surface more tenaciously than on bimetallic Pt–Re surfaces. © 1989

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### 1. INTRODUCTION

The platinum–rhenium bimetallic catalyst has been used extensively in the petroleum industry for hydrocarbon reforming (conversion to high-octane fuels) since it was introduced in 1968 (1). Despite its economic importance, 20 years of research has still not conclusively shown why the Pt–Re bimetallic catalyst is superior to the monometallic platinum catalyst. The nature of the interaction between the platinum and the rhenium metals has been discussed in

the literature: one of the important questions being argued is whether or not alloying between the two metals is necessary for enhanced activity maintenance to exist (2–12).

There is a large body of evidence showing that forming an alloy between platinum and rhenium is necessary to obtain the best reforming catalyst. It has been suggested that the behavior of the bimetallic catalyst toward hydrogen is modified compared to the monometallic platinum catalyst. Barbier *et al.* and Margitfalvi *et al.* have reported that the presence of rhenium enables the catalyst to bind more hydrogen than the monometallic platinum counterpart (12, 13). However, Carter *et al.* supplied evidence that the bimetallic catalyst binds less hydrogen than the monometallic platinum

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alone catalyst (14). Some deactivation studies seem to show that alloying is important (6, 15, 16). Pacheco and Petersen found that the hydrogen pressure dependence of catalyst fouling from methylcyclohexane was different for the monometallic platinum and the bimetallic Pt-Re catalysts (17, 18). However, Burch and Mitchell support Bertolacinni and Pellet in their suggestion that rhenium alone can destroy coking precursors without alloying with platinum (10, 19).

A series of studies has been performed in this laboratory using well-characterized single-crystal catalysts and surface science techniques. The primary advantage of using single-crystal bimetallic surfaces is that surface science techniques can be utilized to characterize the composition and structure of the surface. Much evidence gathered over the years suggests that single-crystal catalysts can be compared to supported catalysts, especially to catalysts of low dispersion (20, 21). Using surface science techniques, surfaces of known composition can be prepared reproducibly and their properties studied. With low-pressure-high-pressure techniques, the state of the surface following a reaction at atmospheric pressures can also be examined. In this way the quantity and nature of the carbon deposit on a catalyst can be investigated on the metal surface. Carbon deposited on a supported catalyst cannot be studied quite as easily since it may deposit on both the metal and the support.

From previous studies using single-crystal bimetallic surfaces, it has been shown that platinum and rhenium form a surface alloy (22), and that alloys of these metals exhibit modified behavior toward hydrogen and carbon monoxide chemisorption that cannot be explained as a simple combination of the chemisorption behavior of the two metallic components (23).

In this paper the results of catalytic studies of ethane hydrogenolysis over bimetallic platinum-rhenium surfaces are described. The hydrogenolysis of ethane has

been investigated over many metals (24-26) and was used in this study because of the wide differences in activity displayed by platinum and rhenium toward this reaction. The reaction



has been reported by Sinfelt to be much faster over silica-supported rhenium than over platinum (25).

Hydrogenolysis has been reported to be an important reaction pathway, particularly in the absence of presulfiding the Pt-Re catalyst (7). In this paper it will be shown that the activity and the mechanism of ethane hydrogenolysis are under the control of the surface composition of bimetallic platinum-rhenium surfaces. The ethane hydrogenolysis behavior of bimetallic Pt-Re surfaces cannot be explained as a linear combination of the two metallic components, and evidence will be presented to support the existence of an electronic interaction between the two metals. It was also found that the addition of rhenium to a Pt(111) surface removes in large part the sensitivity of the rate of carbon accumulation on the surface to the reaction conditions.

## 2. EXPERIMENTAL

All experiments were performed in a stainless-steel ultrahigh vacuum (UHV) system pumped with a liquid nitrogen trapped diffusion pump; the base pressure obtained was  $1 \times 10^{-9}$  Torr after bakeout. The system was equipped with a four-grid retarding field analyzer used for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), an ion gun for argon ion sputtering, and a quadrupole mass spectrometer for temperature-programmed desorption (TPD). The system was also equipped with an internal isolation (high-pressure) cell that was used as a batch reactor for catalytic experiments performed near atmospheric pressure without exposing the single-crystal surface to the atmo-

sphere after cleaning or before postreaction characterization. This apparatus has been discussed in detail elsewhere (27).

Single crystals were cut to within  $1^\circ$  of the desired orientation and both sides were polished using standard techniques. The areas of the disks were about  $1 \text{ cm}^2$  with a thickness of 0.5 mm. A Pt(111) or Re(0001) crystal was spot welded to platinum wires (0.020 in.) that were spot welded to gold support rods (0.062 in.) affixed to a cooled block at the bottom of the manipulator. The temperature of the crystals was controlled using resistive heating a feedback mechanism monitoring either a 0.005-in. Chromel/Alumel pair or a Pt/10% Rh–Pt pair of thermocouple wires spot welded to the edge of the crystal.

Platinum and rhenium crystals were cleaned by cycles of heating at 1000 K in  $3 \times 10^{-7}$  Torr of oxygen, followed by argon ion sputtering with  $1 \times 10^{-4}$  Torr of argon at 1000 K and a 1-keV beam energy, and annealing at 1300 K until no impurities (mainly Re, Pt, S, Ca, C, O) could be detected by AES. Following crystal cleaning, it was verified that a sharp LEED pattern was obtained corresponding to a  $1 \times 1$  surface structure for Pt(111) and Re(0001). Rhenium was removed from platinum surfaces, and platinum was removed from rhenium surfaces by prolonged argon ion sputtering at room temperature and a 2-keV primary beam energy after carbon had been removed in  $3 \times 10^{-7}$  Torr oxygen at 900 K. Rhenium metal was deposited from a 0.5-mm-diameter rhenium wire heated resistively to 1800–2100 K at a deposition rate of between 1 and 5 min/monolayer. Platinum metal was deposited at a similar rate by heating a coiled 0.5-mm-diameter platinum filament to 1400–1700 K as described previously (22, 28). The Pt(111) crystal was held at room temperature during rhenium deposition and was flashed to 700 K periodically to remove any adsorbed CO and CO<sub>2</sub> that was generated by the rhenium source. Platinum deposition was also performed at room temperature, but flashing the substrate was

unnecessary since significant CO and CO<sub>2</sub> were not generated by the platinum source.

Experiments on bimetallic alloyed surfaces were also performed. To generate this surface, an epitaxial surface was flashed briefly to 850°C. The coverages reported were determined by using AES; the spectra obtained for alloyed surfaces always resembled spectra obtained for epitaxial surfaces. The platinum coverage measured after alloying was also less than the coverage measured of the generating epitaxial surface as expected. However, the first layer composition is unknown because annealing to over 700°C causes diffusion that may result in rhenium atoms becoming exposed at the surface (22).

Following preparation and characterization of a surface, the internal isolation cell was closed and pressurized with reactant gases. Hydrogen and ethane were research purity and obtained from Matheson. The accumulation of products was monitored using a gas chromatograph, and the calculation of the turnover frequencies was carried out assuming that the atomic density of all surfaces was  $1.5 \times 10^{15}$  sites/cm<sup>2</sup>. After completion of a high-pressure reaction, usually 2 hr, the internal isolation cell was evacuated using sorption and liquid nitrogen trapped diffusion pumps. Postreaction surface characterization following ethane hydrogenolysis reactions was performed to determine the carbon accumulation that occurred during reaction.

### 3. RESULTS

#### 3.1. Ethane Hydrogenolysis on Pt(111) and Re(0001) Surfaces

Ethane hydrogenolysis reactions were performed over Pt(111) and Re(0001), and the reaction conditions were as follows:  $P_{\text{H}_2} = 100$  Torr,  $P_{\text{C}_2\text{H}_6} = 10$  Torr, and  $T = 300^\circ\text{C}$ . The initial rate of reaction on clean Pt(111) was  $5 \times 10^{-3}$  CH<sub>4</sub> molecule/site-sec under these conditions. Reactions involving C–C bond breaking are often structure sensitive, and indeed the initial rate of reaction was

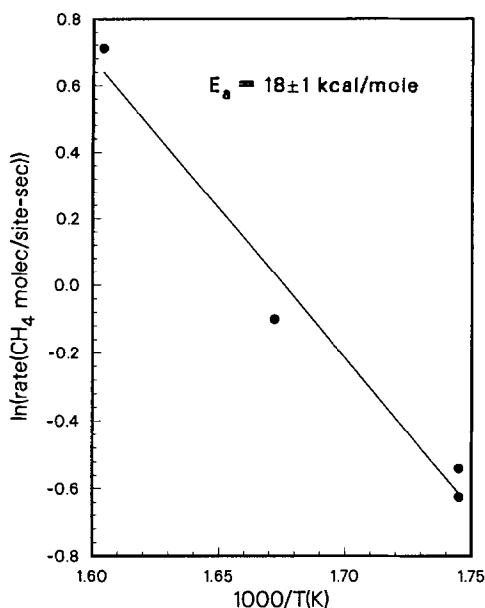


FIG. 1. Activation energy plot for  $C_2H_6$  hydrogenolysis on Re(0001). The reaction conditions were as follows:  $P_{C_2H_6} = 10$  Torr,  $P_{H_2} = 100$  Torr, and the temperature ranged from 300 to 350°C.

increased to 0.07 molecule/site-sec by roughening the surface with argon ion sputtering at room temperature and no annealing.

The activity of a Re(0001) surface was examined, and reactions were carried out under the same conditions as those for Pt(111). The initial rate of methane formation on a clean Re(0001) surface was 0.55  $CH_4$  molecule/site-sec, and again the activity could be increased by roughening the surface with argon ion sputtering at room temperature and no annealing. On the roughened Re(0001) surface, the rate obtained was 1.8 molecules/site-sec.

The activity of a Re(0001) surface was examined between 300 and 350°C, and the results are shown in Fig. 1. An activation energy of  $18 \pm 1$  kcal/mole was obtained at fixed ethane and hydrogen partial pressures.

### 3.2. Rhenium Deposited on Pt(111):

#### Activity vs Re Coverage

With the addition of a small amount of

rhenium to Pt(111), the activity was dramatically increased compared to clean Pt(111) as can be seen in Fig. 2. Even with a rhenium coverage between 0.1 and 0.2 monolayers (ML), the initial rate was two orders of magnitude higher than that of clean Pt(111) and gave an activity equivalent to that obtained on a Re(0001) surface. When two or more monolayers of rhenium were added to a Pt(111) surface, the rate of methane formation was 0.5  $CH_4$  molecule/site-sec. This rate is very close to the rate obtained for a clean Re(0001) surface. At rhenium coverages between 0.6 and 1 ML, a synergistic effect was observed where a maximum rate of methane formation between 2 and 4 molecules/site-sec was obtained, much higher than that on the clean Re(0001) crystal face.

### 3.3 Platinum Deposited on Re(0001):

#### Activity vs Pt Coverage

With the addition of the less active platinum metal to a Re(0001) surface, an enhancement was obtained in the hydrogenolysis rate, reaching a maximum rate of methane formation between 0.3 and 0.5 ML

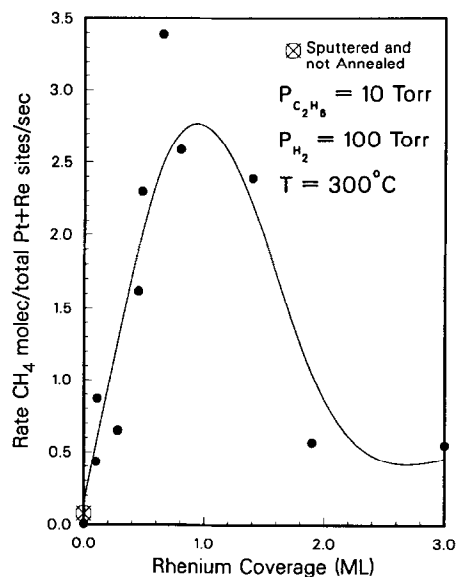


FIG. 2. Ethane hydrogenolysis activity vs rhenium coverage on Pt(111).

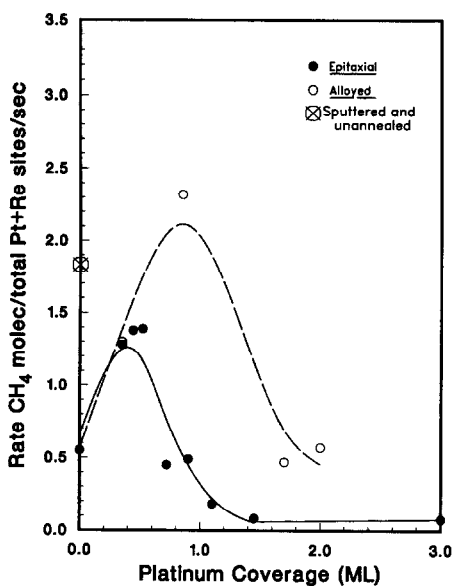


Fig. 3. Ethane hydrogenolysis activity vs platinum coverage on Re(0001). The reaction conditions were as follows:  $P_{C_2H_6} = 10$  Torr,  $P_{H_2} = 100$  Torr, and  $T = 300^\circ\text{C}$ .

platinum. These results are shown in Fig. 3. Even at a platinum coverage of  $\theta_{Pt} \sim 1$  ML, the surface had an activity equivalent to that of the clean Re(0001) surface. The activity of the surface was not observed to be less than that of clean Re(0001) until a second monolayer of platinum was introduced. When the platinum coverage exceeded 1.5 ML, an initial rate of near 0.07 molecule/site-sec was observed, which was equivalent to the rate observed for a roughened Pt(111) surface. The initial rates obtained are summarized in Table 1 for the surfaces discussed.

For the Pt-Re(0001) system, experiments were also performed on alloyed surfaces, i.e., bimetallic surfaces heated above the bulk diffusion threshold which is near  $700^\circ\text{C}$  (22). Alloyed surfaces were found to be quite active. In fact, an alloyed surface composed of 0.9 ML of platinum gave a rate almost five times higher than clean Re(0001) and was also higher than the rate obtained on a roughened Re(0001) surface. An alloyed surface with a composition near

2 ML of platinum was as active as clean Re(0001).

### 3.4. Hydrogen Pressure Dependence

The hydrogen pressure dependence for the ethane hydrogenolysis reaction was previously reported by Sinfelt to be different for platinum and rhenium metals (25). This indicates that a different mechanism may operate on the two surfaces, so experiments were performed to observe how the reaction mechanism might be influenced by the presence of both metals together on a surface.

The reaction conditions used for these experiments were as follows:  $T = 350^\circ\text{C}$ ;  $P_{C_2H_6} = 5$  Torr; and  $P_{H_2} = 520$ – $1035$  Torr. The hydrogen partial pressure dependence of this reaction from three different surfaces is shown in Fig. 5. Using the rate law  $r = kP_{C_2H_6}^n P_{H_2}^m$  for this reaction, the following values were obtained for the hydrogen pressure dependence. For clean Pt(111),  $m$  was  $-2.0 \pm 0.2$ . When the surface was covered with 2 ML of rhenium,  $m$  was found to be  $-0.7 \pm 0.1$ .

The bimetallic surface tested had a rhenium coverage of 0.3 ML. This surface was chosen because it exposed 80% platinum yet it was as active as 2 ML of rhenium on Pt(111) (Fig. 2). The hydrogen pressure dependence obtained from this surface was

TABLE 1

Initial Rates of Ethane Hydrogenolysis Obtained on Pt(111), Re(0001), and Bimetallic Surfaces Derived from These Surfaces

	Clean	Roughened <sup>a</sup>	$\theta_{R_{max}}^b$	$R_{max}^c$	$R(\theta > 1)^d$
Pt(111)	0.005	0.07	0.7	4	0.5
Re(0001)	0.55	1.8	0.4	1.4	0.07

Note. All rates in turnover frequencies (total metal sites-sec)<sup>-1</sup>.

<sup>a</sup> After Ar ion sputtering and no annealing.

<sup>b</sup> Monolayer coverage of other metal at which maximum hydrogenolysis rate occurs. Rates on epitaxial Pt-Re(0001) only.

<sup>c</sup> Maximum rate obtained.

<sup>d</sup> Rate obtained on bimetallic films greater than one monolayer.

TABLE 2

Carbon Accumulation during Ethane Hydrogenolysis Reaction as a Function of Rhenium Coverage and Hydrogen Pressure

Surface: Re monolayers	$P_{H_2}$ (Torr)		
	520	775	1035
Pt(111)	0.4	0.5	0.3
0.3	1.25	1.15	1.25
2	1.5	1.1	0.9

Note.  $T = 350^\circ\text{C}$ ,  $P_{C_2H_6} = 5$  Torr.

similar to that obtained from Pt(111),  $m = -1.8 \pm 0.2$ .

### 3.5. Pt-Re: The State of the Surface following Ethane Hydrogenolysis Reactions

The supported bimetallic Pt-Re catalyst is known to resist deactivation by the accumulation of carbonaceous deposits better than the monometallic platinum catalyst is. Using Auger electron spectroscopy, the accumulation of carbonaceous deposits on the metal surface was measured, and comparisons were made between the surfaces studied.

With rhenium deposited on Pt(111), the amount of carbon remaining on the surface after a 2-hr reaction depended on the reaction conditions, and sometimes on the surface composition as well. When the reaction was carried out at  $300^\circ\text{C}$ , 10 and 100 Torr of ethane and hydrogen, respectively, the carbon accumulation was independent of the surface metals composition. The carbon coverage after 2 hr was  $\theta_C \sim 1.5 \pm 0.3$  ML on all surfaces tested. This is in agreement with results obtained by Zaera and Somorjai (29). At higher temperatures and hydrogen pressures, the amount of carbon accumulated after 2 hr did depend on the metallic surface composition as shown in Table 2. With a temperature of  $350^\circ\text{C}$ , 5 Torr ethane, and higher hydrogen pressures, the following was observed. The three surfaces tested accumulated less car-

bon under these conditions than the corresponding surfaces at  $300^\circ\text{C}$  and 100 Torr hydrogen. The Pt(111) surface accumulated substantially less carbon at the higher temperature and hydrogen pressure. With rhenium present on the surface, the carbon accumulation was only 15–30% less at the higher temperature and hydrogen pressure.

Postreaction characterization was also performed for the Pt-Re(0001) system, and similar results were obtained regarding carbon deposition following ethane hydrogenolysis reactions. However, it had been observed that when several monolayers of rhenium were deposited onto Pt(111), it was easier to remove carbon from the surface following ethane hydrogenolysis reactions. For this reason, the following comparisons were made for the Pt-Re(0001) surface after ethane hydrogenolysis reactions. The amount of carbon left on the surface following reaction ( $\theta_{C1}$ ), and the carbon still remaining following flashing of the surface to 800 K ( $\theta_{C2}$ ), was determined using AES as it had been for the Re-Pt(111) system. Some carbon was observed to

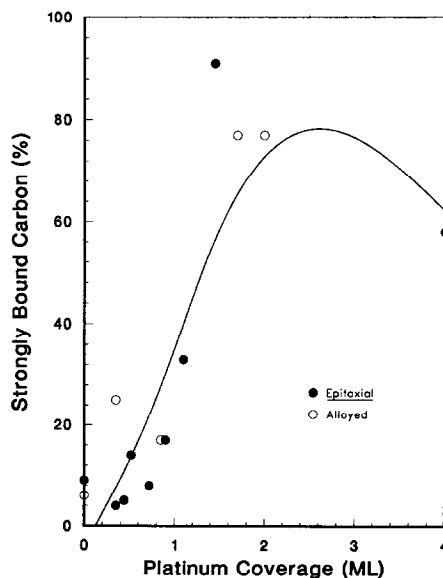


FIG. 4. Irreversibly adsorbed carbon vs platinum coverage on Re(0001). The reaction conditions were the same as those in Fig. 3.

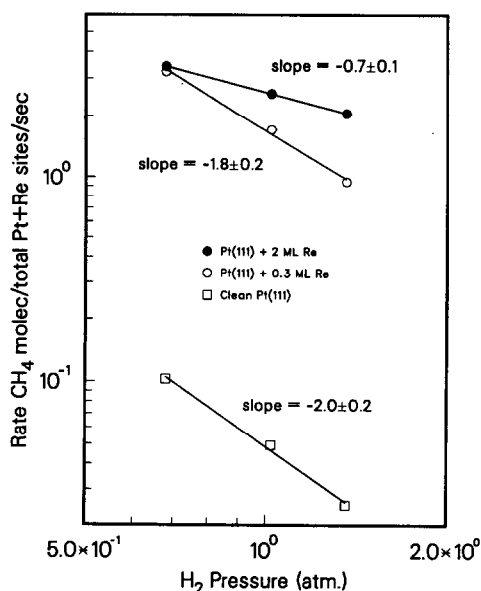


FIG. 5. Hydrogen pressure dependence for ethane hydrogenolysis on Re-Pt(111). The reaction conditions were as follows:  $P_{C_2H_6} = 5$  Torr,  $P_{H_2} = 500$ – $1000$  Torr,  $T = 350^\circ\text{C}$ .

leave the surface during heating since  $\theta_{C_2} < \theta_{C_1}$ . The ratio  $\theta_{C_2}/\theta_{C_1}$  then gives the fraction of irreversibly adsorbed carbon, and this fraction was found to be highest on thick platinum overlayers. The results obtained are shown in Fig. 4.

When the rhenium surface was covered with less than one monolayer of platinum, better than 80% of the carbon desorbed during flashing. With platinum films one to four monolayers thick, only between 10 and 40% of the carbon was found to desorb. These results were similar whether or not the surface was alloyed.

#### 4. DISCUSSION

##### 4.1. Ethane Hydrogenolysis Activity

Large differences in ethane hydrogenolysis activity exist between  $\text{SiO}_2$ -supported platinum and rhenium, and on well-ordered surfaces of platinum and rhenium. Table 3 shows a comparison between some data taken from the literature and from this work (25, 26, 29, 30). It can be seen that large

differences in kinetic parameters exist between platinum and rhenium metals for both supported and unsupported single-crystal catalysts. Some differences were also observed between supported and single-crystal catalysts, but comparison is difficult since the data were collected under different reaction conditions. It is interesting to note that the activation energy of ethane hydrogenolysis is lower on single-crystal surfaces than it is on  $\text{SiO}_2$ -supported catalysts. This indicates that the mechanism of hydrogenolysis is structure sensitive and may depend on the size of the ensemble available on the surface. It is also possible that the support plays an important role in the reaction.

The ethane hydrogenolysis activity over platinum was low under the conditions used. However, when rhenium was added to the surface the hydrogenolysis activity increased, and near one-third of a monolayer of rhenium, the activity was close to the activity of a Re(0001) surface (Fig. 2). A surface with a rhenium coverage between  $0.3 < \theta_{\text{Re}} < 1$  monolayer displayed an activity greater than a Re(0001) surface, and a maximum rate of  $\text{CH}_4$  formation was obtained near two-thirds of a monolayer. This suggests that a mixed metal site with a stoichiometry of  $\text{Re}_2\text{Pt}$  is the best hydrogenolysis site. One explanation for the higher

TABLE 3

Summary of Kinetic Parameters for Ethane Hydrogenolysis over  $\text{SiO}_2$  Supported and Single-Crystal Re and Pt Metals

Metal	Temp. range ( $^\circ\text{C}$ )	$E^a$	Order in ethane ( $n$ )	Order in hydrogen ( $m$ )	Temp. ( $^\circ\text{C}$ ) <sup>b</sup>
Re <sup>c</sup>	229–265	31	0.5	+0.3	250
Pt <sup>c</sup>	344–385	54	0.9	-2.5	357
Pt(111)	200–350	34 <sup>d</sup>	—	-2.0 <sup>e</sup>	350
Re(0001)	300–350	18 <sup>e</sup>	—	—	—
0.3 ML Re-Pt(111)	—	—	—	-1.8 <sup>e</sup>	350
2 ML Re-Pt(111)	—	—	—	-0.7 <sup>e</sup>	350

Note. The rate law is given by  $r = kP_{C_2H_6}^n P_{H_2}^m$ .

<sup>a</sup> Apparent activation energy (kcal/mole).

<sup>b</sup> Temperature at which the reaction orders were determined.

<sup>c</sup> From Ref. (25).

<sup>d</sup> From Ref. (29).

<sup>e</sup> This work.

rates observed on a mixed Pt–Re ensemble is that of an electronic interaction between the two metals that strongly influences the catalytic activity. This will be discussed later.

Another possibility is that the reaction is structure sensitive, and less coordinated rhenium atoms exposed on the surface may be more active to account for the higher activity. This explanation is plausible because ethane hydrogenolysis was found to be structure sensitive over both platinum and rhenium; roughened crystal surfaces were found to be about 3.5 and 10 times more active than well-annealed surfaces of Re(0001) and Pt(111), respectively.

To explore whether an electronic effect was responsible for the hydrogenolysis enhancement of a mixed ensemble, experiments were performed on the Re(0001) basal plane and bimetallic platinum–rhenium surfaces derived from this surface. When the less active platinum metal is added to a rhenium surface, the activity should drop unless an electronic effect is operating. It was found that after depositing platinum on the Re(0001) surface an increase in hydrogenolysis activity was observed (Fig. 3). An explanation invoking a roughened surface can be discarded because a roughened Pt(111) surface is still an order of magnitude less active than a Re(0001) surface, so an increase in activity by the addition of platinum to the Re(0001) surface cannot be attributed solely to an increase in defect sites on the surface. For Pt–Re(0001) surfaces a maximum rate of methane formation was observed close to one-third of a platinum monolayer, suggesting that a mixed site of the stoichiometry of  $\text{Re}_2\text{Pt}$ , as was found for Re–Pt(111), provides the best hydrogenolysis site. A possible explanation not requiring a charge transfer is that hydrogenolysis occurs on the rhenium sites and that the role of platinum is to provide a source of adsorbed hydrogen atoms. Although this explanation is appealing, it cannot explain how a rhenium surface covered with a monolayer of plati-

num had an activity quite close to that of the clean Re(0001) activity. This interesting fact demonstrates that a single monolayer of platinum can make a good cracking catalyst when perturbed by an underlying rhenium substrate and, we believe, is clear proof that a charge redistribution occurs between the two metals when they are in intimate contact. Previous studies have also provided evidence for an electronic interaction between the two metals (22, 23).

When bimetallic Pt–Re(0001) surfaces were annealed to 1150 K, an even larger enhancement was observed for the ethane hydrogenolysis reaction. The reason is that upon annealing to 1150 K, either a more active alloy is formed or platinum diffuses underneath the surface layer exposing rhenium atoms on the surface. In either case these rhenium atoms with platinum ligands seem to be very active for ethane hydrogenolysis. The converse is also true, demonstrating that one metal perturbs the other metal when they are in intimate contact, i.e., when they are nearest neighbors.

The hydrogenolysis activity of the Pt–Re(0001) surface was lowered by adding a second platinum layer. This indicates that the perturbation or ligand effect does not extend to second nearest neighbors. This phenomenon was also observed for the Re–Pt(111) surface since two monolayers of rhenium on Pt(111) gave a hydrogenolysis rate similar to that of a Re(0001) surface.

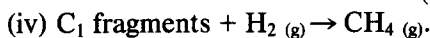
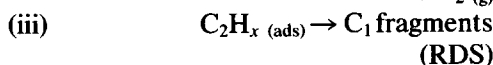
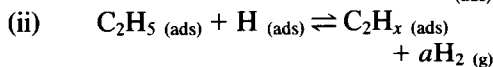
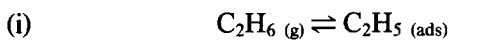
As studies progressed on the platinum–rhenium system, it was found that catalytic hydrogenolysis reactions were more sensitive than AES to the presence of trace amounts of platinum on rhenium or of rhenium on platinum. Trace amounts of adsorbate could sometimes be undetected using AES yet cause an unexpectedly high hydrogenolysis rate. Sometimes after a control reaction was initiated on an assumed monometallic substrate (platinum or rhenium), it became apparent that the surfaces had not been cleaned thoroughly enough, and the reaction would have to be aborted. Argon ion sputtering was usually performed for at



least 2 hr at room temperature to ensure that all of the adsorbate metal was removed. Bertolacinni and Pellet carried out experiments where physical mixtures of monometallic platinum-rhenium catalysts were prepared and apparently performed as well as codeposited catalysts. They failed to detect cross contamination between the platinum and the rhenium metals on their physically mixed catalysts, but perhaps enough occurred to partially change the performance of the catalyst (10).

#### 4.2. Hydrogen Pressure Dependence for Ethane Hydrogenolysis on Re-Pt(111)

Experiments were performed to explore the hydrogen partial pressure dependence of ethane hydrogenolysis reactions over platinum, rhenium, and bimetallic Pt-Re surfaces. The hydrogen pressure dependence was different on rhenium and platinum surfaces in agreement with Sinfelt (25), and the values obtained for the order in hydrogen pressure was  $-0.7$  and  $-2$  for Pt(111) and 2 ML Re-Pt(111), respectively. A negative order in hydrogen pressure may be due to a competitive adsorption of hydrogen, and perhaps to the formation of dehydrogenated species that are the hydrogenolysis precursors. A model was presented recently by Sinfelt to describe the ethane hydrogenolysis reaction over several metals (26):



According to this model, the concentration and the stoichiometry of the cracking precursor,  $C_2H_x$ , are characteristic of the metal. The nature of the metal and the hydrogen pressure controls the equilibrium, hence the concentration of the cracking precursor.

Rhenium alone is the better cracking catalyst while platinum alone is known to be the better hydrogenation/dehydrogenation catalyst. However, when both metals were present together on the surface, an even better cracking catalyst was obtained. Why this occurs and how the hydrogen pressure dependence of the bimetallic surface is related to the pressure dependencies of Pt(111) and Re(0001) alone were explored.

To answer these questions, a bimetallic surface composed of 0.3 ML of rhenium on Pt(111) was selected because it had an activity similar to that of the Re(0001) surface. When the hydrogen pressure dependence of this surface was measured, it was found to be  $-1.8 \pm 0.2$ , and close to the value obtained for the Pt(111) surface. The addition of 0.3 ML of rhenium to a Pt(111) surface resulted in a catalyst that was as active as a monometallic Re(0001) surface, yet displayed a hydrogen pressure dependence that was close to the value obtained for Pt(111). One explanation for this is as follows. The model assumed that breaking of the C-C bond is rate limiting, so the rate depends on the surface concentration of the  $C_2H_x$  precursor. Although rhenium can catalyze the breaking of this bond readily, equilibrium may not favor a high concentration of the cracking precursor on this surface. In addition, higher hydrogen pressures lower the concentration of this precursor. However, the presence of platinum alters the surface so that the equilibrium is shifted to a more dehydrogenated  $C_2H_x$  species which is readily cracked. This shift in equilibrium is shown by the order in hydrogen pressure obtained on the bimetallic 0.3 ML Re-Pt(111) surface that approaches the order obtained for the monometallic Pt(111) surface. It may also be that the cracking precursor on the bimetallic surface resembles the precursor obtained on the platinum surface rather than that obtained on the rhenium surface.

Another explanation is possible along these lines. The order in hydrogen obtained for the Re(0001) surface is less negative

than the order obtained for Pt(111). An increase in hydrogen pressure results in a decrease in concentration of  $C_2H_x$  fragments, resulting in a negative contribution to the hydrogen pressure dependence as discussed above. However, it is possible that on rhenium the hydrogenation rate of  $C_1$  fragments is similar to the rate of cracking the  $C_2H_x$  fragment. If this were so, the rate of hydrogenation of  $C_1$  fragments to methane would increase with hydrogen pressure, and the contribution to the hydrogen pressure dependence of this step would be positive. With the two opposing contributions operating, the net result is a hydrogen pressure dependence for rhenium that is less negative than that for platinum. The reason that the bimetallic 0.3 ML Re-Pt(111) surface has a hydrogen pressure dependence resembling platinum is that the presence of platinum on the surface increases the availability of hydrogen to hydrogenate and remove  $C_1$  fragments from the surface.

In support of this argument, it was previously shown that a bimetallic Re-Pt(111) surface with a rhenium coverage of  $\theta_{Re} \sim 0.3$  ML could adsorb more hydrogen with a smaller hydrogen-metal bond strength than clean Pt(111). This indicates that the bimetallic surface has a larger hydrogen reservoir and can exchange it more readily, so that the decrease in activity caused by diluting the active rhenium with the relatively inactive platinum is offset by the greater surface hydrogen made available by the presence of platinum.

#### 4.3. Accumulation of Carbonaceous Deposits

When the rates obtained from different surfaces were compared, initial rates were used so that differences in the development of the carbonaceous residues was minimized. However, measurements made of the carbon accumulation on the surface after 2 hr of reaction time did present interesting results.

At 300°C and 100 Torr of hydrogen, the carbon accumulation did not depend on the metallic composition of the surface. Under more severe conditions, 350°C and 500–1000 Torr of hydrogen, the rhenium surface and the bimetallic surface accumulated slightly less carbon. The magnitude of the effect was not large enough to suggest any change in the reaction pathway compared to reactions carried out at the lower temperature and hydrogen pressure. The platinum surface, on the other hand, accumulated 75% less carbon at the higher temperature and hydrogen pressure. Although the accumulation of carbonaceous deposits was lower under these conditions, the hydrogenolysis rates of the Pt(111) surface was two orders of magnitude lower than those of the other two surfaces, similar to the difference in hydrogenolysis rates observed between platinum surfaces and surfaces exposing rhenium under the lower temperature and hydrogen pressures. This suggests that two reaction pathways exist, one leading to hydrogenolysis and the formation of methane, and the other leading to the formation of carbonaceous deposits. The pathway leading to the formation of carbonaceous deposits on platinum is more sensitive to changes in reaction conditions than it is on rhenium or bimetallic Pt-Re surfaces. This is consistent with observations made by Pacheco and Petersen for methylcyclohexane deactivation of platinum and bimetallic Pt-Re surfaces. They found that the hydrogen pressure dependence was much more negative on platinum than it was on bimetallic Pt-Re catalysts (i.e.,  $-5.5$  and  $-1.3$  for Pt and Pt-Re, respectively) (17, 18). It was also found that when platinum atoms have rhenium ligands, they bind carbonaceous deposits less tenaciously than platinum atoms without an underlying rhenium layer. Apparently bimetallic surfaces can tolerate higher levels of carbon on the surface because a larger portion of these deposits is reversibly adsorbed compared to monometallic platinum.

## 5. CONCLUSIONS

Using the hydrogenolysis of ethane as a probe reaction on bimetallic surfaces of platinum and rhenium, it has been shown that an electronic effect exists between the two metals resulting in a hydrogenolysis activity larger than that displayed by either monometallic component alone. This result cannot be explained as a linear combination of the activity of the two components. The best hydrogenolysis catalyst was a surface having a  $\text{Re}_2\text{Pt}$  stoichiometry.

A bimetallic 0.3 ML  $\text{Re-Pt(111)}$  surface has a hydrogen partial pressure dependence that is similar to the  $\text{Pt(111)}$  surface, yet an activity that is close to that of a  $\text{Re(0001)}$  surface. This may be related to previous results that showed a 0.3 ML  $\text{Re-Pt(111)}$  surface binds more hydrogen than either  $\text{Pt(111)}$  or  $\text{Re(0001)}$  surfaces.

The accumulation of carbonaceous deposits was more sensitive to reaction conditions on monometallic  $\text{Pt(111)}$  than it was on rhenium or  $\text{Pt-Re}$  surfaces, and the deposits formed on platinum surfaces were adsorbed more strongly than those on bimetallic  $\text{Pt-Re}$  surfaces.

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