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The Effects of Rhenium and Sulfur on the Reactivity and Selectivity of Pt Single-Crystal Catalysts

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Platinum–rhenium bimetallic surfaces have been prepared by condensing Re on Pt(111) crystal surfaces in ultrahigh vacuum (UHV) using a pulsed metal vapor vacuum arc plasma gun. Conversion reactions of *n*-hexane and cyclohexane have been studied. The same reactions were also performed over sulfided surfaces made by depositing atomic sulfur on the metal in UHV. The presence of Re on Pt(111) greatly increases the hydrogenolysis of *n*-hexane. Sulfiding of the catalysts suppresses hydrogenolysis and enhances the cyclization activity of *n*-hexane toward methylcyclopentane. The maximum reactivity for cyclization to form five-membered rings over the sulfided Pt–Re surfaces is obtained when the Pt surface is covered by 1 monolayer (ML) of Re. When the Pt(111) surface is covered by 1 ML of Re, the sulfided catalyst is twice as active as the unsulfided catalyst for cyclization of *n*-hexane. Presulfiding also enhances the dehydrogenation activity of cyclohexane over the Pt–Re bimetallic surfaces. In that case, maximum reactivity of sulfided catalysts is observed when the Pt surface is covered by 0.5 ML of Re. We conclude that the Pt–Re bimetallic catalyst shows its unique properties when it is combined with sulfur.

INTRODUCTION

The development of the Pt–Re bimetallic reforming catalyst in the late sixties (*1*) was one of the breakthroughs in the history of transition metal catalyst development (*2*). The presence of Re in the bimetallic system significantly enhanced the stability and reactivity of the catalyst. Since then, many bimetallic reforming catalysts have been studied and developed, including Pt–Ir (*3*), Pt–Sn (*4*), Pt–Rh (*5*), Pt–Ni (*6*), Pt–Te/Se (*7*), Pt–Au (*8*), Pt–Cu (*9*), and Pt–Fe (*10*). The Pt–Re bimetallic catalysts show unique properties when they are combined with sulfur. Because of the high hydrogenolysis activity of Re, the pure Pt–Re alloy does not function as a naphtha reforming catalyst and sulfiding of the catalyst is critical. The sulfiding process had been used in reforming catalysts to suppress the initial hydrogenolysis activity of fresh catalysts by poisoning the active hydrogenolysis sites. However, the role of sulfur in the Pt–Re catalysts is more than just to poison the active sites for hydrogenolysis as revealed by studies of the Pt–Re system in the presence of sulfur (*11–15*). Shortly after his invention of the Pt–Re bimetallic reforming catalyst, Kluksdahl showed (*11*) that sulfiding of the catalyst prior to reforming significantly decreased the deactivation rate of the Pt–Re catalyst. Sachtler and co-workers proposed that sulfur divides the Pt–Re surface into small Pt ensembles by forming stable Re–S bonds and these ReS_x species suppress the conversion of the carbonaceous species into harmful graphitic carbon layer, resulting in enhanced activity maintenance (ensemble size effect) (*12, 13*). den Hartog *et al.* (*14*) showed that sulfidation of the $Pt–Re/Al_2O_3$ catalysts increased the relative role of acid-catalyzed reactions. A "ligand effect" was proposed by Barbier and co-workers (*15*); sulfur, as an electron acceptor, changes the electronic density of the unpoisoned metallic surface area, resulting in the change of the selectivity and activity of the catalysts.

We have been studying catalytic reactions using well-characterized single-crystal

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model catalysts and surface science techniques (*16*). The advantage of using low-surface-area single-crystal catalysts is that surface science techniques can be utilized to characterize the composition and structure of the catalyst surface. By utilizing surface science techniques, known surface composition and structure can be prepared and reproduced for catalytic studies. Another advantage of this technique is that we can use simplified model catalysts; we can study the interaction between metals or metal and other components, and we can study the effect of each component on catalytic reactions separately. In this paper, we report the effect of Re and sulfur on hydrocarbon conversion reactions over the Pt model catalysts. The Pt–Re–S catalyst system was produced and the conversion of *n*-hexane and cyclohexane was studied in the absence of alumina support which is usually employed for the Pt–Re catalysts.

EXPERIMENTAL

All experiments were performed in a stainless-steel ultrahigh-vacuum (UHV) system equipped with an Auger electron spectrometer (AES), a low-energy electron diffraction (LEED) optics, a quadrupole mass spectrometer, and an internal isolation cell for catalytic reactions. This system is also equipped with a metal deposition source and a solid-state electrochemical sulfur source. After the preparation and characterization of the catalysts in UHV, the internal isolation cell was closed and pressurized with reactants for reaction studies. The accumulation of products was monitored using a gas chromatograph and the turnover rate was determined assuming that the atomic density of all surfaces was 1.5 × 10^{15} sites/cm^2. This UHV/high-pressure reactor system has been described in detail elsewhere (*17*).

Preparation of Catalysts

A platinum single crystal, which was cut to (111) orientation and polished using standard techniques, was used as a catalyst. The platinum sample was cleaned using cycles of oxygen treatment at 1000 K, Ar ion sputtering at 900 K, and annealing at 1300 K until no impurities could be detected by AES.

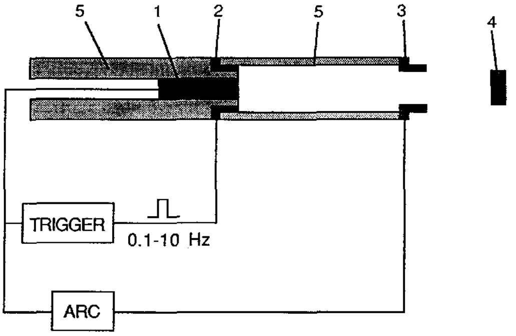

FIG. 1. Schematic drawing of a pulsed metal vapor vacuum arc plasma gun. (1) Cathode (Re). (2) Trigger. (3) Anode. (4) Substrate (Pt). (5) Insulator (alumina).

Bimetallic surfaces were prepared by depositing Re on Pt(111) in UHV with a pulsed *Me*tal *V*apor *V*acuum *A*rc plasma gun (MEVVA) (Fig. 1). The MEVVA source, which was originally developed at the Lawrence Berkeley Laboratory (*18*), was especially designed to deposit a precise amount of refractory metals, ranging from submonolayer to tens of monolayers. A schematic drawing of the source is shown in Fig. 1. The cathode, which is the material to be deposited (Re), is biased by several hundred volts and the stainless-steel anode is grounded. The dense metal plasma, formed by arc discharge, plumes away from the cathode toward the substrate (Pt), which is in front of the anode. The arc discharge is driven by a simple L–C pulse line of impedance 1 ohm and pulse length 250 μs. The line is charged up to several hundred volts with a dc power supply. The arc discharge is initiated by a high-voltage (15 kV) pulse applied to a trigger electrode. The spark plasma formed between coaxial electrode and the central cathode closes the main anode–cathode circuit, which causes the formation of the main metal plasma between the cathode and anode. The principle of operation of the MEVVA source has been fully

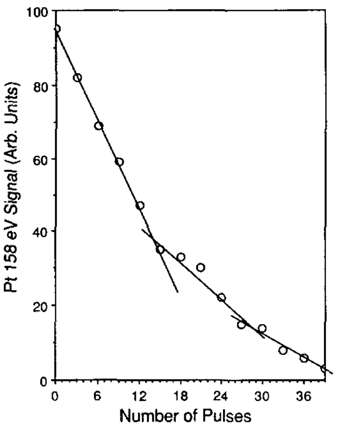

FIG. 2. Rhenium uptake on Pt(111). Breaks near 14 shots and 28 shots correspond to the completion of the first and second monolayers of Re.

described elsewhere (*19, 20*). The deposition rate can be controlled by changing the pulse rate. Auger uptake results show that Re grows layer-by-layer on Pt(111) (Fig. 2). LEED studies indicated that deposited Re on Pt(111) forms the p(1 × 1) structure regardless of the coverage. We obtained similar results when we used the resistively heated Re filament as a Re source (*21*).

To prepare a sulfided catalyst, atomic sulfur was deposited in UHV using a solid-state electrochemical cell (Pt/Ag/AgI/Ag_2S/Pt) described by Hayek and co-workers (*22*). Saturation amount of sulfur was used for sulfiding in all cases. Figure 3 shows the process of catalyst preparation schematically.

The Surface Structure and Composition of the Catalysts during and after the Reaction

It is not possible to analyze the surface of the catalysts during the actual catalytic process in our system. However, we believe the coverage of Re does not change during the reaction because bulk diffusion of Re into Pt did not take place up to 500°C in vacuum and the coverage of Re was unchanged after the reaction. Preadsorbed sulfur, however, desorbed during the reaction. After 2 h of reaction the coverage of sulfur decreased to 0.1–0.3 ML from the initial saturation coverage (ca. 0.7 ML) and the Pt–Re bimetallic surfaces retained more sulfur than pure Pt. To minimize the effect of surface structure and composition change during the reaction, we used the initial turnover rate to compare the performance of the catalysts. It may be possible to estimate the coverage of sulfur and carbon after the reaction from the Auger spectra. However, this had too much scatter to provide meaningful data because both Pt and Re peaks in the Auger spectrum were heavily attenuated by intense sulfur and carbon peaks.

RESULTS

Conversion of n-Hexane over Pt(111)/Re and Pt(111)/Re/S

Conversion of *n*-hexane was performed over Pt(111) using 20 Torr of *n*-hexane and 200 Torr of hydrogen at 300°C. After 2 h of reaction on Pt(111) total conversion was about 1% and the product was composed of methylcyclopentane (cyclization, 50%), C_1–C_5 hydrocarbons (hydrogenolysis,

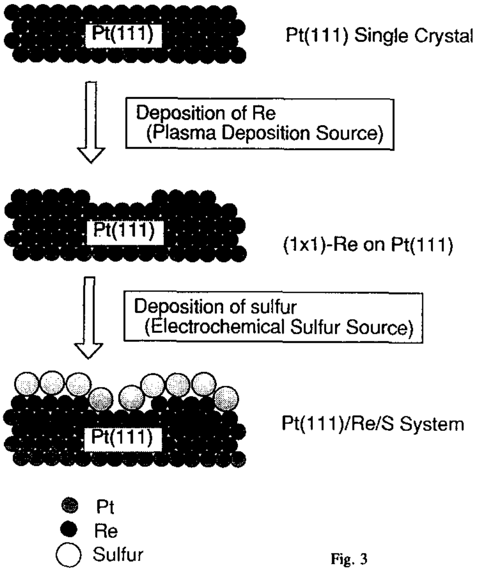

Fig. 3

FIG. 3. The schematic diagram of the preparation of sulfided bimetallic catalysts.

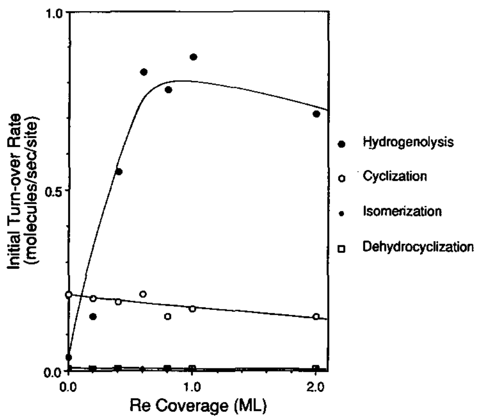

FIG. 4. Rate of n-hexane conversion on Pt(111) as a function of Re coverage. Reaction conditions: T = 300°C, $P_{n\text{-hexane}}$ = 20 Torr, and P_{H_2} = 200 Torr.

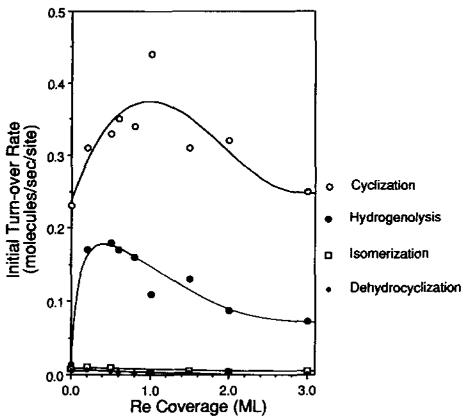

FIG. 5. Rate of n-hexane conversion on sulfided Pt(111) as a function of Re coverage. Reaction conditions: T = 300°C, $P_{n\text{-hexane}}$ = 20 Torr, and P_{H_2} = 200 Torr. The catalysts were sulfided by depositing saturation amount of sulfur.

32%), 2- and 3-methylpentane (isomerization, 14%), and a small amount of benzene (dehydrocyclization, 4%, by molar ratio). The effect of Re coverage on Pt(111) on the reactivity and selectivity of n-hexane conversion was determined. The presence of Re on Pt(111) increased hydrogenolysis activity enormously (Fig. 4). The initial turnover rate for hydrogenolysis increased from 0.038 molecules/s/site to 0.87 molecules/s/site when the Pt(111) surface was covered by 1 ML of Re. Cyclization activity decreased as Re coverage increased. Isomerization and dehydrocyclization activities were too low to be compared meaningfully.

Initial sulfiding changed the selectivity of the catalysts. The most significant change was a decrease in hydrogenolysis activity and an increase in cyclization activity (Fig. 5). By sulfidation, hydrogenolysis activity over the Pt(111) surface covered by 1 ML of Re dropped from 0.87 to 0.11 molecules/s/site, and cyclization activity over the same surface increased from 0.17 to 0.4 molecules/s/site. When the Pt–Re bimetallic surfaces were sulfided, maximum rates for hydrogenolysis and cyclization were observed when the Pt surface was covered by 0.5 ML of Re and 1 ML of Re, respectively. Figure 6 shows the difference between sulfided and unsulfided Pt–Re catalysts toward cyclization of n-hexane to methylcyclopentane. In the case of unsulfided catalysts, the addition of Re on Pt(111) decreased cyclization activity. However, sulfidation of the catalyst increased the cyclization activity and the max-

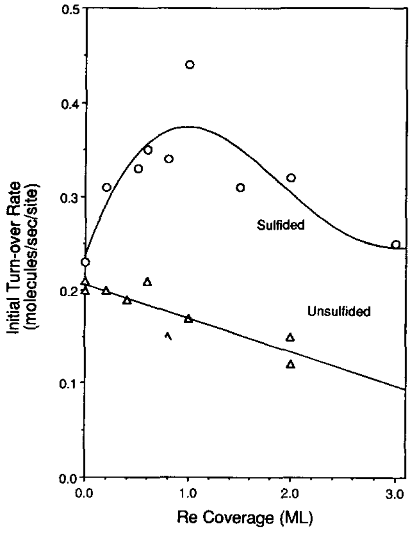

FIG. 6. Cyclization of n-hexane on sulfided and unsulfided Pt–Re surfaces. Reaction conditions: T = 300°C, $P_{n\text{-hexane}}$ = 20 Torr, and P_{H_2} = 200 Torr.

TABLE 1

Comparison of Initial Turnover Rates for *n*-Hexane Conversion

Catalysts	Initial turnover rate (molecules/s/site)			
	Cyclization	Hydrogenolysis	Isomerization	Dehydrocyclization
Clean Pt(111)	0.21	0.038	0.009	0.004
Pt(111) + 1 ML Re (unsulfided)	0.17	0.87	0.003	0.004
Pt(111) + 1 ML Re (sulfided)	0.44	0.11	0.003	0.003

Note. Reaction conditions: $T = 300°C$, $P_{n\text{-hexane}} = 20$ Torr, $P_{H_2} = 200$ Torr.

imum activity was observed when the surface was covered by 1 ML of Re. When the Pt surface was covered by 1 ML of Re, the sulfided catalyst was twice as reactive as the unsulfided catalyst. Table 1 summarizes the initial turnover rates for the conversion of *n*-hexane on clean Pt(111), Pt(111) with 1 ML of Re and sulfided Pt(111) with 1 ML of Re.

Conversion of Cyclohexane over Pt(111)/Re and Pt(111)/Re/S

Conversion of cyclohexane over the Pt–Re catalysts was performed under the same reaction conditions for *n*-hexane conversion; $P_{\text{cyclohexane}} = 20$ Torr, $P_{\text{hydrogen}} = 200$ Torr, and temperature = 300°C. After 2 h of reaction over the clean Pt(111) surface, total conversion was 23% with 99.99% of product being benzene. The addition of Re to the Pt(111) surface decreased dehydrogenation activity and slightly increased hydrogenolysis activity (Fig. 7). However, hydrogenolysis products formed only 10% of the total product even after the Pt surface was covered by 1.5 ML of Re. Sulfiding of the Pt–Re catalysts suppressed hydrogenolysis and increased dehydrogenation rates of cyclohexane to benzene. The maximum rate of dehydrogenation was obtained when the Pt surface was covered by approximately 0.5 ML of Re and was sulfided. Table 2 summarizes the initial turnover rates for the conversion of cyclohexane on clean Pt(111), Pt(111) with 0.4 ML of Re, and sulfided Pt(111) with 0.4 ML of Re.

DISCUSSION

The hydrogenolysis of hydrocarbons, in the range of C_2–C_8, over Pt–Re bimetallic catalysts has been studied extensively (*23–25*). Due to lower activation energy of hydrogenolysis over the Re catalysts (*26*), the Pt–Re catalysts show high hydrogenolysis activity. It has been generally found that the Pt–Re bimetallic catalysts show higher hydrogenolysis activity than the physical mixture of Pt and Re (*27*). It is well known that sulfur selectively poisons the hydrogenolysis activity of hydrocarbon conversion catalysts (*24*). Our model catalysts also show that the addition of Re on Pt(111) increases hydrogenolysis and coadsorbed sulfur selectively suppresses the hydrogenolysis of *n*-hexane (Figs. 4 and 5). However, it is a quite unusual result that coadsorbed sulfur enhances the activity of cyclization of *n*-hexane over Pt–Re catalysts (Fig. 6). This result shows that sulfur not only changes the selectivity of the catalyst by selective poisoning but enhances the reactivity. One possible explanation stems from the competition between the two different reactions, hydrogenolysis and cyclization. Over sulfided catalysts, adsorbed hydrocarbon species have a greater proba-

TABLE 2

Comparison of Initial Turnover Rates for Cyclohexane Conversion

Catalysis	Initial turnover rates (molecules/s/sites)	
	Dehydrogenation	Hydrogenolysis
Clean Pt(111)	11.5	0.007
Pt(111) + 0.4 ML Re (unsulfided)	11.2	0.45
Pt(111) + 0.4 ML Re (sulfided)	17.5	0.05

Note. Reaction conditions: $T = 300°\mathrm{C}$, $P_{\mathrm{cyclohexane}} = 20$ Torr, $P_{\mathrm{H}_2} = 200$ Torr.

bility to form cyclic molecules because hydrogenolysis activity is suppressed. This argument is especially applicable to the case of the conversion of *n*-hexane over the Pt–Re catalysts, on which hydrogenolysis is a dominant reaction.

The selective formation of methylcyclopentane over benzene is an important result. This is the first report of sulfided Pt–Re bimetallic system producing five-membered cyclic molecules over six-membered rings, almost exclusively. Since the sulfided Pt–Re system on alumina is well-recognized for its superior aromatization (dehydrocyclization) activity, our model Pt–Re–S system is clearly different from that used in the petroleum refining technology. Either the unique preparation of our catalysts is responsible for the enhanced selectivity for methylcyclopentane formation or the requirement of the presence of alumina is implicated with ring enlargement of the five-membered cyclic molecules to six-membered rings followed by dehydrogenation to benzene.

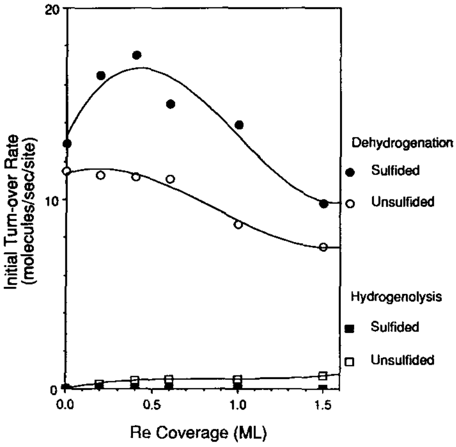

FIG. 7. Rate of cyclohexane conversion on sulfided and unsulfided Pt(111) as a function of Re coverage. Reaction conditions: $T = 300°\mathrm{C}$, $P_{\mathrm{cyclohexane}} = 20$ Torr, and $P_{\mathrm{H}_2} = 200$ Torr. Sulfided catalysts were made by depositing saturation amount of sulfur before the reaction.

The conversion of cyclohexane to benzene on Pt–Re catalysts, where hydrogenolysis is insignificant, also shows enhancement of the dehydrogenation activity by sulfur (Fig. 7). The activity enhancement can be explained by reduced hydrogen coverage over the sulfided surfaces. The presence of coadsorbed sulfur reduces the hydrogen coverage over the catalyst. Then the cyclohexane–benzene equilibrium is shifted in the direction of benzene. The result is the increased dehydrogenation rate of cyclohexane on sulfided surfaces of Pt–Re.

As our results of the effects of sulfiding Pt–Re show, the reactivity of the catalyst is greater than the linear combination of the activities of the two components, Pt and Re. The Pt–Re–S catalysts show the maximum reactivity when the Pt surface is covered by certain amount of Re; 1.0 ML of Re for cyclization of *n*-hexane toward methylcyclopentane and 0.5 ML of Re for dehydrogenation of cyclohexane toward benzene. There is the possibility that the effective surface area of Pt is increased by deposition of Re. However, titration by CO TPD shows that the effective area for CO adsorption decreases as Re coverage increases. It is not unusual that the reactivity of the bimetallic catalyst is more than the linear combination of the activity of the two components. Hydrogenolysis of ethane over Pt–Re bimetallic catalysts showed the highest activity when the Pt surface was covered by 1 ML of Re (*25*) and hydrogenation of CO_2 to methane on Rh showed the highest activity when the Rh surface was covered by 0.5 ML of titania (TiO_x) (*28*).

Our investigation continues to probe the reason for the formation of methylcyclopentane from *n*-hexane instead of benzene over this modified bimetallic system.

CONCLUSION

It has been found that coadsorbed sulfur suppresses the hydrogenolysis of *n*-hexane and cyclohexane over the Pt–Re bimetallic catalysts. It has also been found that sulfur enhances the cyclization of *n*-hexane to methylcyclopentane almost exclusively and the dehydrogenation of cyclohexane over the Pt–Re catalysts. The enhancement in activity by sulfur was greatest when the Pt surface was covered by 1 ML of Re for *n*-hexane cyclization and 0.5 ML for cyclohexane dehydrogenation. It has been proposed that an interaction among Pt, Re, and S, in addition to structural poisoning by sulfur, is responsible for the nonlinear catalytic behavior.

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