Ensemble size reduction by rhenium–sulfur as a method to lower the rate of deactivation of hydrocarbon reactions over Pt catalysts

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The reactions of cyclohexane (6.7 kPa) and *n*-hexane (13.3 kPa) in H_2 (450 kPa) were studied on platinum–rhenium model catalysts in the range 570–740 K. The catalysts were prepared by depositing rhenium on a platinum foil or platinum on a rhenium foil. The catalyst total area was 0.5–1.0 cm^2. The surfaces were pre-sulfided before reaction and thiophene added to the feed to maintain the surface sulfided under reaction conditions. Sulfur binds with rhenium forming a catalytically inactive rhenium–sulfur compound. As the concentration of rhenium–sulfur on the surface is increased and the platinum ensembles become smaller, only dehydrogenation–hydrogenation activity is observed. However, the catalyst becomes more resistant to deactivation.

Keywords: platinum catalyst; effect of iridium, rhenium, and sulfur; reforming reactions; hydrocarbon reactions; deactivation on platinum

1. Introduction

Catalytic reforming is a high volume process in the oil industry employed to convert low into high octane naphthas. One of the major advances in catalytic technologies was the introduction of a reforming catalyst composed of platinum supported on acidic alumina. For the next generation of catalysts, platinum was substituted by bimetallic Pt–Re, Pt–Ir, and Pt–Sn which exhibited higher resistance to deactivation [1]. The first bimetallic system to be reported, more than 25 years ago, was Pt–Re [2]. In spite of a constant effort, as measured by the number of scientific publications, it is still not clear why this system is more stable than platinum in its catalytic activity and how does it function as compared to platinum. The models proposed in the literature for explaining the role of rhenium include the stabilization of platinum crystallites against sintering using rhenium as an anchor [3], formation of a catalytically active rhenium compound with the alumina [4], alloying of rhenium with platinum [5], and interaction of the alloy with sulfur [6–11]. The last model proposed that sulfur binds with rhenium and forms an inactive rhenium–sulfur compound. This model is also supported in this letter. One possible reason for so many models in the literature is that the industrial catalyst is composed of less than one percent by weight of each metal component on a high surface area oxide, which makes the identification and preparation of surface phases very difficult. Also, the overall reforming reactions involve not only the metal sites but the acid sites on the support as well, which adds to the complexity of the problem.

One way to study this problem is to prepare model catalysts on single crystal foils or thin films of area of about 1 cm^2, where the various components of the catalyst can be studied separately [12]. This approach has been used successfully for platinum single crystals with different crystallographic orientations [13] and also in studies of the Pt–Re bimetallic system [14–16]. The model system approach has also been applied to supported catalysts [17].

The main objective of this letter is to summarize the mode of action of platinum–rhenium catalysts as compared to platinum. Under the reaction conditions carried out in this study most of the rhenium remained sulfided forming a compound with no catalytic activity. This compound diluted the platinum ensembles, with the sulfur sticking out of the surface and forming a physical barrier that inhibited the growth of large domains of carbonaceous deposits. It was found that the stability of the catalyst increased as the amount of rhenium–sulfur on the surface was increased. Also, as the concentration of rhenium–sulfur increased no large ensembles of platinum were left and only dehydrogenation–hydrogenation activity remained. It appears therefore that for a sulfided Pt–Re catalyst the production of aromatic, cyclic, and isomerized molecules from linear alkanes will be carried out with the help from the acidic support through a bifunctional mechanism where the metal part provides mainly dehydrogenation–hydrogenation activity. A more detailed account of Pt–Re catalysts will be published elsewhere [18]. This mode of action where one of the components is inactive does not seem to apply to all reforming bimetallic catalysts. Preliminary results on the Pt–Ir system [19] suggest that the mode of action of iridium is to promote the platinum by increasing the turnover rate per total metal on the surface for isomerization and dehydrocyclization. The promotion mechanisms of iridium and rhenium on platinum appear to be very different.

2. Experimental

The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 1.0×10^{-7} Pa (7.5×10^{-10} Torr) and equipped with a containment cell capable of enclosing the sample and holding a maximum pressure of 2 MPa (20 atm). The containment cell was connected to an external loop containing a gas compressor (Whitey, LC-10) for the gas recirculation, forming a batch reactor with a total reactor volume of 460 cm^3. The flow rate in the reaction was estimated from the manufacture's charts to be about 15 cm^3 s^{-1}. This flow rate permitted a conversion per pass of less than 0.02%. The sample was heated resistively and the temperature was measured through a thermocouple type K spot-welded on the center upper edge of the foil.

The catalysts used in this study were polycrystalline metal foils. The platinum foil was 0.076 mm thick with a total surface area of 0.5–1 cm^2 and with a purity of 99.95% (Lawrence Berkeley Laboratory pool stock). The rhenium foil was 0.1 mm thick, had a total surface area of 0.5 cm^2 and a purity of 99.99% (Johnson Matthey).

Both sides of the platinum and rhenium foils were cleaned by cycles of Ar sputtering at room temperature at 2 keV, O_2 treatment at 1000 K and 6.7×10^{-5} Pa (5×10^{-7} Torr), and annealing at 1173 K until the AES spectra showed no foreign peaks. After each reaction studied, which involved the deposition of rhenium or iridium over the platinum foil or vice versa, Ar sputtering for 1 h on each side followed by annealing at 1173 K was sufficient (as shown by AES) to free the surface from the deposited metal.

The deposition of rhenium and iridium on the platinum foil or platinum on a rhenium foil, was accomplished by a metal vapor vacuum arc plasma (MEVVA) source. The operation and principle of this device has been described before [20]. The pre-sulfided samples were prepared by saturation with atomic sulfur generated on a solid-state electrochemical cell (Pt/Ag/AgI/Ag_2S/Pt) [21].

The samples for reaction studies were prepared as follows. After cleaning and annealing, the desired amount of metal was deposited and the sample was immediately sulfided to the saturation coverage amount with atomic sulfur. The sample was then annealed at 1000 K for 1 min and sulfur was deposited again at room temperature to replenish any lost sulfur during the annealing treatment. Finally, the sample was heated to 800 K for 5 min with the sulfur source still on.

The reaction rate measurements were made on a batch mode. The hydrocarbons *n*-hexane (Fluka, puriss), neopentane (Phillips, research grade, 99.8%) and cyclohexane (Fluka, puriss) were degassed by freeze–thaw cycles. The hydrocarbons were introduced before H_2 (Matheson, prepurified). Most of the experiments were run with 6.7 or 13.3 kPa (50 or 100 Torr) of hydrocarbon and 450 kPa (3300 Torr) of H_2. The reactant mixture was circulated for 20 min before the foil was heated to the reaction temperature. The reaction products were analyzed by a gas chromatograph (Hewlett-Packard 5890-II) with a flame ionization detector. The products were separated on a 50 m long, 0.2 mm diameter column (Pona). The first analysis was done after 3 min of reaction and subsequent analyses were carried out at intervals of 10–15 min. A typical accumulation versus time plot is shown in fig. 1 for the reaction with cyclohexane. Although the number of turnovers is very high at the end of the experiments, the total conversion was lower than 1.5%, which accounts for the pseudo-zero-order kinetics. The initial turnover rate was calculated from the slopes at time zero. Rates will be reported as nominal turnover rates and as turnover rates. The nominal turnover rate includes all surface atoms as active sites. The turnover rate includes only the surface platinum atoms. To

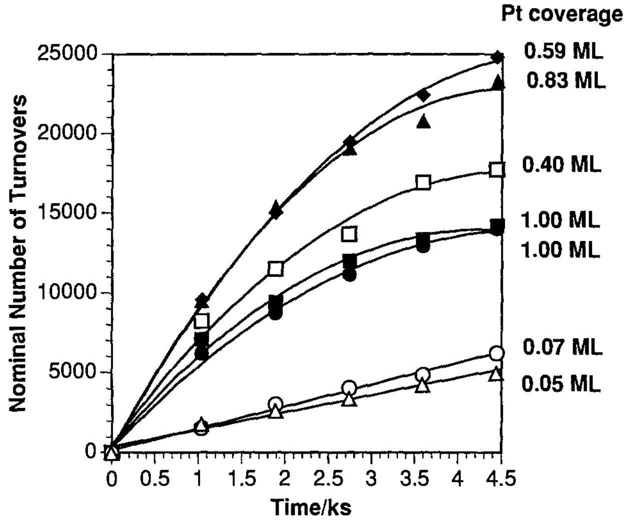

Fig. 1. Number of cyclohexane molecules converted to benzene per surface atom (platinum and rhenium) as a function of time. Reaction run on a sulfided platinum foil with different amounts of deposited rhenium at 6.7 kPa of cyclohexane, 450 kPa of H_2, and 573 K. The platinum coverages were 1.0 ML (■), 1.0 ML (●), 0.83 ML (▲), 0.59 ML (◆), 0.40 ML (□), 0.07 ML (○), and 0.05 ML(△).

measure the amount of platinum on the surface of the model catalysts two probe reactions were used. The isomerization of neopentane to isopentane was used on Pt–Re catalysts and the dehydrogenation of *n*-hexane to 1-hexene on Pt–Ir catalysts. The isomerization of neopentane is characteristic of a few noble metals [22] and does not occur to any extent on rhenium. The isomerization can occur by a bond-shift [23] or metallacyclobutane mechanism [24,25]. The number of sites required on a bond-shift mechanism is three [26] and only one based on a metallacyclobutane mechanism [27]. Thus, it was possible to probe the amount of platinum on the surface even at high dilution. It was assumed that the fraction of neopentane reacting through each mechanism will remain the same as the sizes of the platinum ensembles are decreased. For the platinum–iridium catalysts the reaction of dehydrogenation of *n*-hexane to 1-hexene was found to be much slower on iridium than on platinum. This difference in rate permitted us to correlate the initial rates of dehydrogenation with the amount of platinum on the surface. An atom surface density of 1.0×10^{15} atoms cm^{-2} was used in the rate calculations.

On the reaction of cyclohexane dehydrogenation, after the sulfidation step the sample was heated to 800 K in 450 kPa of H_2 for 1 min to remove sulfur bound to platinum. The reason for this treatment was that the lower reaction temperature in this reaction (573 K) might not be sufficient to remove most of the sulfur adsorbed on platinum.

Blank experiments were run to certify that no background catalytic activity was present. Those experiments were run on a sulfided rhenium foil at the same reaction conditions used in the experiments. On the reactions with *n*-hexane and cyclohexane no reaction products were observed after 1 h and up to the maximum reaction temperature of 800 and 570 K, respectively. These experiments also establish that Re–S is catalytically inactive.

3. Results and discussion

One of the key reactions in reforming is dehydrogenation–hydrogenation. It occurs exclusively on the metal sites and forms the olefin intermediates that will further react at the acidic sites of the support and then return to the metal for hydrogenation. As a model for this reaction, the dehydrogenation of cyclohexane to benzene in the presence of H_2 at 673 K was studied. Fig. 1 shows the accumulation plots for this reaction for a platinum foil with different amounts of rhenium–sulfur on the surface. As the amount of platinum on the surface is decreased, there is less curvature on the accumulation plots which is an indication that the catalyst deactivates less. This resistance to deactivation is confirmed by re-charging the reactor and re-starting the reaction: the samples showed the same initial nominal turnover rate on the second run as the rate obtained at the final of the first run. Thus, as suggested by the slope at the end of the reaction in fig. 1, the sample with no rhenium–sulfur on it will show virtually no activity on the second run while the sample with 0.05 monolayers of platinum will show the same constant rate as on the first run. It is then clear that the amount of deactivation on the sample is a function of the amount of rhenium–sulfur on the surface which in turn determines the size of the platinum ensembles. Another feature in fig. 1 is that the initial rate should decrease as the amount of platinum on the surface is decreased but it initially increases (0.40–0.83 ML Pt). This is at first surprising since a sulfided rhenium foil showed no activity for this reaction. This behavior points to the promoting effect of rhenium–sulfur on platinum. The explanation for this effect can be better seen in fig. 2, where the turnover rate, but not the nominal turnover rate, is plotted. In this case, the initial turnover rate obtained from fig. 1 and normalized to the number of platinum atoms on the surface, should be constant since the dehydrogenation of cyclohexane to benzene is a structure insensitive reaction. Instead, the turnover rate increases as the amount of rhenium is increased until it reaches a constant value at about half a monolayer. At this point, the curvature on the accumulation plots (fig. 1) also decreases. This behavior indicates that the catalyst has always the same turnover rate per platinum atom except when it deactivates too fast for an initial rate to be measured. The curvature in the plots in fig. 1 and the constant turnover in fig. 2 suggest that rhenium–sulfur prevents the poisoning of the platinum foil. The lower rates on the platinum foil are due to poisoning by carbon deposits.

Reactions other than dehydrogenation also occur over platinum without assistance from the support. As an example, *n*-hexane can be dehydrocyclized to benzene, cracked to lower hydrocarbons, isomerized to 2- and 3-methylpentane or

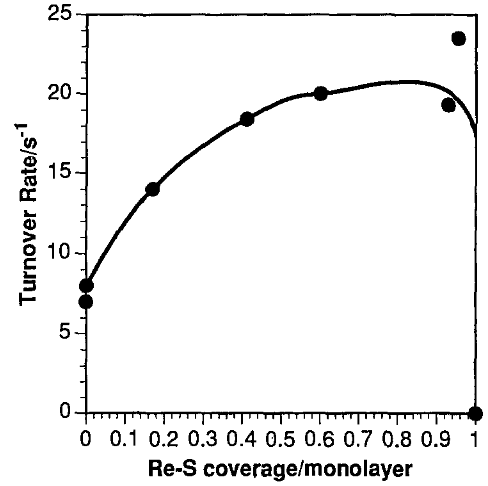

Fig. 2. Number of cyclohexane molecules converted to benzene per platinum atom per second. Reaction run on a sulfided platinum foil with different amounts of deposited rhenium at 6.7 kPa of cyclohexane, 450 kPa of H_2, and 573 K. Number of platinum atoms measured by reactions with neopentane.

cyclized to methylcyclopentane [26,28]. The selectivity for these reactions will depend among other factors on the size of the platinum ensembles. The largest sites are required for the reactions of dehydrocyclization and hydrogenolysis and the smallest sites (possibly only one atom) are required for dehydrogenation–hydrogenation. The addition of rhenium–sulfur lowers the rates of the reactions that require large ensembles. These trends are shown in fig. 3. The rate of the hydrogen-

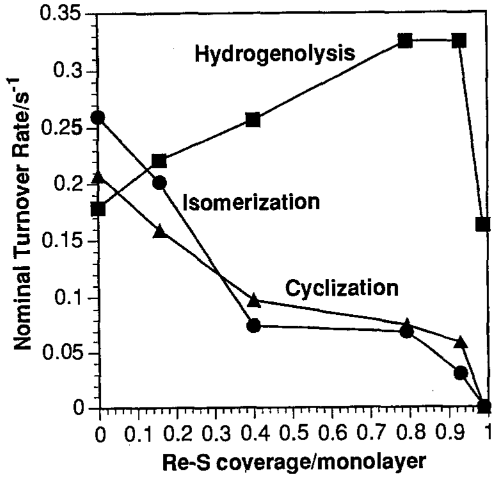

Fig. 3. Number of *n*-hexane molecules converted per surface metal atom (platinum and rhenium) per second to hydrogenolysis products (■), 2- and 3-methylpentane (isomerization), (●), and methylcyclopentane (cyclization) (▲), as a function of rhenium–sulfur coverage. Reaction run on a sulfided platinum foil at 13.3 kPa of *n*-hexane, 450 kPa of H_2, 10 ppm of thiophene and 740 K.

olysis reaction actually increases with rhenium coverage but that is because rhenium is a very active metal for hydrogenolysis unless it is capped with sulfur. Under reaction conditions some sulfur is lost exposing some of the rhenium atoms, which forms with platinum a very active bimetallic hydrogenolysis catalyst [15,29]. For the isomerization and cyclization reactions, however, rhenium is inactive and the reaction rates decreased as the amount of rhenium is increased.

For the dehydrogenation reactions a different trend is observed (fig. 4). The turnover rate for the dehydrogenation of *n*-hexane to 1-hexene increases as the amount of rhenium is increased. This result is similar to the one obtained for the dehydrogenation of cyclohexane, where the rate also increases with rhenium–sulfur coverage, but in the *n*-hexane case the turnover rate does not reach a maximum. To understand this trend it should be mentioned first that the reaction temperature and hydrocarbon to hydrogen ratio for the reactions of *n*-hexane are higher than for the reaction of cyclohexane which will increase the rate of deactivation. In fact, the deactivation is so drastic in the reaction of *n*-hexane that the turnover rate did not reach a constant value but continued to increase as the platinum ensembles become smaller. A similar dehydrogenation rate is obtained if platinum is deposited on a rhenium foil (fig. 4). Again, the difference in rates for the different compositions are due to deactivation of the samples. This effect was confirmed by running the reaction a second time and observing that the initial rates decreased more on the samples with higher amounts of platinum [18].

The picture that emerges from this data is one where small ensembles of platinum surrounded by rhenium–sulfur resist deactivation much better than larger ensembles. The reason for this improvement, as suggested in the literature before

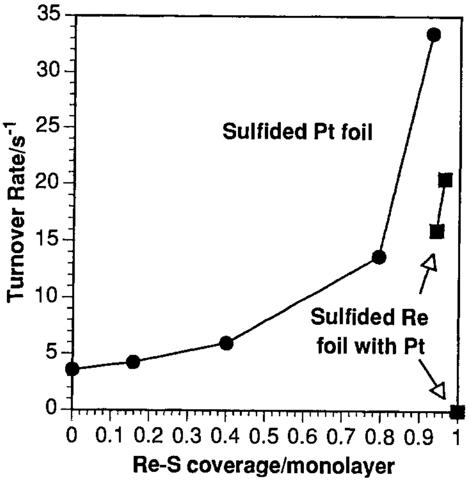

Fig. 4. Number of *n*-hexane molecules converted to 1-hexene per platinum atom per second. Rates on a sulfided platinum foil as a function of deposited rhenium (●), or on a sulfided rhenium foil as a function of deposited platinum (■). Reaction run at 13.3 kPa of *n*-hexane, 450 kPa of H_2, 10 ppm of thiophene and 740 K. Number of surface platinum atoms measured by reactions with neopentane.

[6–10], is that the sulfur atoms binding to rhenium will form physical barriers around the platinum clusters that will make difficult for hydrocarbon fragments to diffuse and meet at a platinum site where they will further dehydrogenate forming a coke-like residue that will impede further adsorption on these sites. It must be pointed out that the range of high concentration of rhenium–sulfur the only chemistry left on the platinum surface will be dehydrogenation–hydrogenation reactions. A compromise between resistance to deactivation and the desired selectivity on the platinum surface must be met in choosing the amount of rhenium on the catalyst.

In the case of Pt–Ir alloys the role of iridium on increasing the catalyst stability may be different from rhenium–sulfur, since iridium is a noble metal with a surface chemistry similar to platinum. In this case, a synergism between platinum and iridium may happen in the same way as in the case of the rate acceleration for hydrocarbon hydrogenolysis reactions on sulfur free platinum–rhenium [15,29]. Indeed, preliminary results suggest that sulfided platinum–iridium catalysts are not as resistant to deactivation as platinum–rhenium catalysts when the experiments are carried out under the conditions where platinum–rhenium showed superior performance to platinum. However, the effect of iridium can be measured if the catalyst is not presulfided and the experiments are carried out at conditions where it will not deactivate drastically (higher H_2 pressure (890 kPa H_2) and lower reaction temperature (715 K)). Fig. 5 shows that as the amount of iridium is increased, the turnover rates of isomerization and cyclization go through a maximum while the rate of hydrogenolysis increases monotonically. Since this bimetallic catalyst is more active than platinum alone, a lower temperature of operation, which will translate

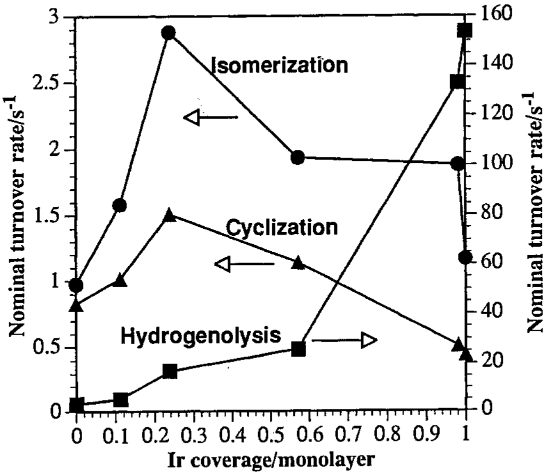

Fig. 5. Number of *n*-hexane molecules converted per surface metal atom (platinum and iridium) per second to hydrogenolysis products (■), 2- and 3-methylpentane (isomerization) (●), and methylcyclopentane (cyclization) (▲), as a function of iridium coverage. Reaction run on a platinum foil at 13.3 kPa of *n*-hexane, 890 kPa of H_2, and 715 K. Number of surface platinum atoms measured by the rate of dehydrogenation of *n*-hexane to 1-hexene.

into a longer life, might be used. One obvious problem of this catalyst is the undesirable high rate of hydrogenolysis. However, the hydrogenolysis rate decreases faster than the rates of other reactions as the catalyst ages since larger sites are required for hydrogenolysis. Also, the hydrogenolysis rate can be toned down by the use of sulfur containing compounds present in the feed.

Finally, it should be emphasized that, although the same reaction conditions as used industrially can be used on model catalysts, the model catalyst studied here is not a small scale copy of the industrial catalyst. The industrial catalyst is composed of metal crystallites on the nanometer range occupying about 1% of the area of the support, while the model catalyst is a continuous metal surface. This difference seems to be very important in determining the catalyst deactivation rate by carbon deposits [30] because on supported catalysts hydrocarbon fragments can spillover to the support. Thus, it is not expected that the model catalysts tested here will deactivate at the same rate as the industrial ones, but it is expected that they will deactivate by the same mechanism. This difference in rate of deactivation is compensated by our ability to carry out surface composition and structure analysis of model catalysts with greater ease than on the industrial catalysts.

4. Conclusion

The addition of rhenium–sulfur to a platinum catalyst increases its resistance to deactivation by carbon deposits. The most stable catalysts have the smallest platinum ensembles. Depending on the size of the ensembles, the reactions characteristic of platinum will be decreased, with ensembles capable only to carry out dehydrogenation left at high concentrations of rhenium–sulfur. The mechanism for the catalyst stabilization seems to be due to protection of platinum sites by the formation of physical barriers by rhenium–sulfur. Rhenium–sulfur makes it difficult for molecular fragments to diffuse to platinum sites and further dehydrogenate there to form high molecular weight deactivating carbonaceous deposits.

Preliminary data for the Pt–Ir system indicates that for this system adsorbed sulfur does not play the same role as it does in the Pt–Re system. Iridium participates in the surface chemistry, making the catalyst more active for isomerization and cyclization than platinum alone.

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