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Fouling of a Platinum–Rhenium Reforming Catalyst Using Model Reforming Reactions

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It is well known that rhenium stabilizes a commercial platinum reforming catalyst; however, the exact role of Re is still in doubt. The function of Re was investigated by determining and then comparing the fouling characteristics of two model reforming reactions catalyzed by bifunctional Pt and Pt–Re catalysts. The methylcyclohexane (MCH) dehydrogenation reaction was used to probe for changes in the metallic function and the methylcyclopentane (MCP) dehydroisomerization reaction was used to determine variations in the acidic function. Both sulfided and unsulfided catalysts were investigated. Presulfiding either a Pt or Pt–Re catalyst altered significantly the observed reaction rates and deactivation characteristics of the metallic function. The addition of Re to a Pt reforming catalyst greatly reduced the rate of those structure-sensitive secondary reactions catalyzed by the metallic function: toluene dealkylation, MCP ring opening, and long-term MCH fouling. The addition of Re, however, did not affect the structure-insensitive MCH reaction or the initial MCP fouling rate; also, little or no affect was noted in the MCP fouling characteristics. The results presented suggest that there is a metal–metal interaction between Pt and Re.

INTRODUCTION

In the late sixties rhenium was added to the then standard commercial platinum reforming catalyst. This addition greatly stabilized the catalyst during operation. Since then a number of articles have addressed the question of how rhenium actually accomplishes this stabilization. Most of these articles concern themselves with the physical oxidation state of the dual metals (*1–9*) or the effect of rhenium on initial catalytic reaction rates (*10–12*). Articles authored by researchers at various commercial catalyst producers compare the deactivation characteristics of both mono- and bimetallic reforming catalysts during fouling tests with a naphtha feed (*13–16*), but little or no work has been published that compares the fouling characteristics of the above catalysts using model reforming reactions. Accordingly, the objective of this paper is to compare the fouling characteristics of a chlorinated bifunctional Pt–Re reforming catalyst to those of a comparable Pt reforming catalyst using model reforming reactions.

In commercial operation, catalyst presulfidation with hydrogen sulfide has been shown to be not only desirable but necessary even though it lowers the initial catalytic reforming activity (*12, 17–20*). In the absence of a hydrogen sulfide pretreatment step, sulfidation of a reforming catalyst would eventually occur because the feed contains small amounts of sulfur. It is therefore necessary to determine the self-deactivation characteristics of sulfided as well as unsulfided catalysts.

EXPERIMENTAL

The model reforming reactions used in this study are the dehydrogenation of methylcyclohexane (MCH) to toluene and the dehydroisomerization of methylcyclopentane (MCP) to benzene. Dehydrogenation of the cyclohexane ring uses only the metallic Pt function of these bifunctional catalysts (*21, 22*) and is thought to be structure insensitive for a supported Pt catalyst (*21, 22*). The dehydrogenation of MCH is very selective for the formation of toluene, in excess of 95%, and will serve as a probe

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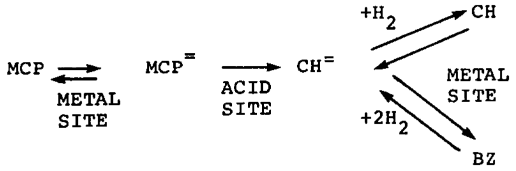
to see if the addition of rhenium affects the fouling characteristics of the metallic function of these catalysts.

The dehydroisomerization of MCP to benzene utilizes both metallic and acidic sites of a bifunctional reforming catalyst and proceeds through a methylcyclopentene, MCP^{2-}, intermediate (*20, 24–28*).



Ring enlargement from MCP^{2-} to cyclohexene, CH^{2-}, on an acidic site is thought to be the controlling step in this sequential reaction (*20, 27, 29*). This reaction is viewed as a means to detect the effect of rhenium on the support.

Deactivation results reported in this study were determined in an experimental apparatus capable of maintaining constant reactant and product concentrations during a deactivation run and has an overall time constant of 4 s. Jossens and Petersen describe this apparatus and the procedure for its operation in detail elsewhere (*30, 31*).

Prior to each experimental run the following *in situ* catalyst pretreatment procedure was followed: fresh catalyst was initially heated from room temperature to 500°C in a flowing stream of helium, calcined for 4 h in a flowing stream of gas containing 100 Torr oxygen with the balance being nitrogen, cooled for 2 h to reducing temperature in a flowing stream of helium, and reduced for 15 h in a flowing stream of hydrogen. The reducing temperature was 475°C except for those MCH deactivation experiments using a Pt catalyst where the temperature was 360°C. Sulfidation of either catalyst, when specified, was performed after the reduction period. Here, a reduced catalyst was sulfided with 3.5 molecules of hydrogen sulfide per platinum atom at 425°C in a flowing stream of hydrogen at atmospheric pressure.

Catalyst samples were obtained from two separate lots each having approximately 0.6 wt% Cl on a γ-alumina support and metal weight percentage loadings of 0.34% Pt and 0.29% Pt–0.3% Re, respectively. For the 88-μm particles used in this study, the effectiveness factor was greater than 0.9 (*30*).

RESULTS AND DISCUSSION

Metallic Site Probe—MCH Initial Rate Kinetics

The intrinsic dehydrogenation–hydrogenation activity of bulk Pt differs significantly from that of bulk Re. At 165°C, Kubicka (*32*) reports that reaction rates for the hydrogenation of benzene over bulk Pt are approximately three orders of magnitude greater than that for Re. Betizeau *et al.* (*11*) in their work on a series of co-impregnated Pt–Re catalysts indicate that the dehydrogenation of 1,1,3-trimethylcyclohexane is 45 times faster on a Pt catalyst than on a Re catalyst at 312°C. In our work we see little difference in the overall catalytic activity between a nominal 0.3% Pt catalyst and a nominal 0.3% Pt–0.3% Re catalyst. What difference that does exist, Pt–Re catalyst being slightly less active, could be attributed to the lower real Pt content of the Pt–Re catalyst.

Observed MCH dehydrogenation kinetics for a Pt–Re catalyst are the same as those for a Pt catalyst. Both catalysts exhibit linear MCH kinetics at low MCH concentration (less than 6×10^{-7} g mole/cm^3, 23. Torr at 352°C) and demonstrate the same inverse toluene kinetics. Toluene inhibition data can be described by a power law expression. The reaction order at 400 Torr hydrogen and 352°C is a negative 0.33 for both catalysts, at 376°C this order changes to a negative 0.6 but approaches zero when hydrogen pressure is increased to 1 atm. An extended discussion of initial MCH dehydrogenation reaction rates over a supported Pt catalyst is presented by Jossens and Petersen (*31*).

The Arrhenius plot in Fig. 1 displays the

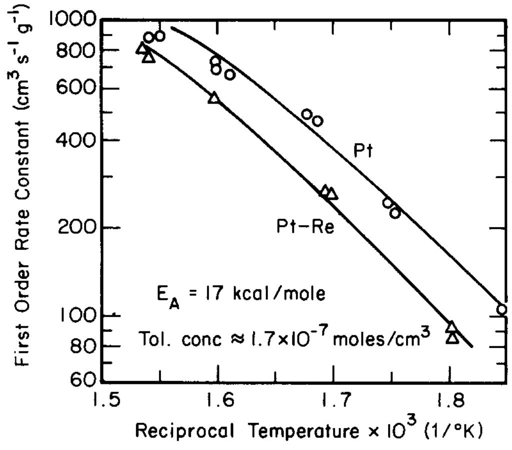


FIG. 1. Arrhenius plot for MCH initial rate kinetics at 405 Torr H_2.

effect of temperature on the dehydrogenation reaction rates for these two catalysts. Both catalysts exhibit the same thermal characteristics with an apparent energy of activation of about 17 kcal/g mole at 352°C.

Sulfidation of a reduced Pt or a Pt–Re catalyst decreases observed initial dehydrogenation reaction rates. Part of the loss in catalytic activity is reversible in a flowing stream of hydrogen while the other part is irreversible. These reversible–irreversible sulfur poisoning characteristics are noted by Menon and Prasad (*12*) in their work on the effect of thiophene on the dehydrogenation of cyclohexane while evidence for reversible poisoning by hydrogen sulfide is given by Hettinger *et al.* (*33*) and Cecil *et al.* (*16*).

The effect of a hydrogen sulfide pretreatment step on the dehydrogenation of MCH is presented in Fig. 2 for the Pt and the Pt–Re catalysts. The reduced catalyst was presulfided at 425°C by adding small aliquots of a 1030-ppm H_2S–H_2 gas to a flowing stream of hydrogen. After each sulfidation step the catalytic MCH dehydrogenation activity was monitored at 20-min intervals until the observed activity reached a constant level. Specifically, the activity was measured at 377°C and 400 Torr hydrogen by adding MCH for 15 s to the pretreatment feed and measuring the reaction rate at the end of this time. Any deactivation resulting from MCH fouling under these conditions is completely reversible. The loss of initial activity due to presulfiding, as shown in Fig. 2, is irreversible; even after 13 h at 377°C and 400 Torr hydrogen, no change in the resulting activity was detected. Reversible losses in catalytic activity for either a Pt or a Pt–Re catalyst are not shown here but were observed for additional hydrogen sulfide aliquots in excess of that required to produce the knee in either curve. Approximately 3.5 atoms of hydrogen sulfide per Pt were added in the pretreatment gas stream; however, the actual fraction of sulfur on either catalyst was not determined in this study.

Figure 2 also shows that the Pt–Re catalyst is more sensitive to hydrogen sulfide than the Pt catalyst. This is consistent with the operational policy of a commercial reforming facility where the maximum allowable sulfur level in the feed is greater when using a Pt catalyst compared to a Pt–Re catalyst (*16*).

Catalyst presulfiding enhances reforming selectivities for either a Pt or a Pt–Re catalyst (*12, 17, 18*). Enhancement in reforming selectivities is also observed by just the addition of Re to a Pt catalyst. For the dehydrogenation of MCH, dealkylation of toluene is the significant secondary reaction

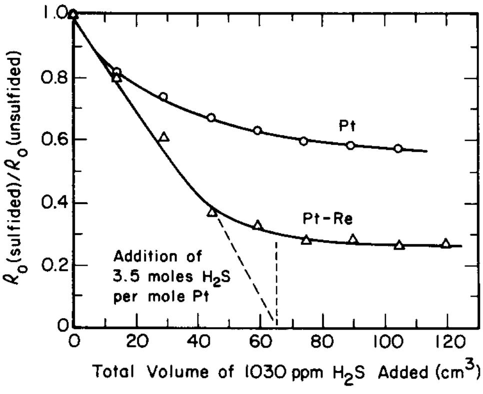


FIG. 2. Irreversible reduction in MCH dehydrogenation activity due to a hydrogen sulfide pretreatment step; equal Pt loading, 425°C.

and occurs on the metallic sites of these bifunctional catalysts. For this reaction the Pt–Re catalyst is less than half as active as the Pt catalyst even though these catalysts have the same dehydrogenation activity.

Rhenium is a stronger hydrogenolysis catalyst than Pt. Sinfelt (*34*) in his comparison of metallic ethane hydrogenolysis catalysts reports that supported Re is five orders of magnitude more active than supported Pt at 205°C. Similarly, Betizeau *et al.* (*11*) show that Re is three orders of magnitude more active for butane hydrogenolysis at 240°C. Contrary to the paraffin hydrogenolysis patterns, Pt is a better dealkylation catalyst than Re at low hydrogen partial pressures. Grenoble (*35*) reports that Pt is nine times more active than for Re for the dealkylation of toluene under conditions which closely approximate our reference reaction conditions. Due to the low dealkylation activity of Re under the reference reaction conditions the presence of bulk Re in a Pt–Re reforming catalyst should add little to the overall dealkylation rate under our reference condition.

Fouling by MCH Dehydrogenation

The fouling characteristics of a Pt and a Pt–Re catalyst accompanying the dehydrogenation of MCH are compared in this section. Results for unsulfided and sulfided catalysts are presented. The characteristics of an unsulfided Pt catalyst are used as the basis for comparison.

An extended discussion of the fouling characteristics resulting from the dehydrogenation of MCH over an unsulfided Pt catalyst is presented in Ref. (*31*). Briefly, this work showed that the deactivation proceeds by at least a two-step mechanism. The first step lasts some 40 min after the initiation of the deactivation experiment and has the following traits: 7 kcal/g mole energy of activation, very slight dependency on reaction rate, a strong dependency on hydrogen partial pressure, and totally reversible in a flowing stream of hydrogen under reaction conditions. Deactivation during this step can be modeled as the establishment of equilibrium between active sites and reversibly poisoned sites. The final equilibrium expression has the form

$$\left[\frac{1 - \langle a_{\mathrm{INT}}\rangle}{\langle a_{\mathrm{INT}}\rangle}\right][\mathrm{H_2}] = K. \tag{1}$$

The term a_{INT} is the hypothetical catalytic activity defined for the endpoint of the initial deactivation step. It is obtained by extrapolating results for the second deactivation step back to zero time. Activity is defined as the ratio of the dehydrogenation reaction rate at a specified time, $\mathcal{R}$, to the initial dehydrogenation reaction rate, $\mathcal{R}_0$. Dehydrogenation reaction rate is measured as the summation of toluene and benzene production rates. The term, $[1 - \langle a_{\mathrm{INT}}\rangle]$, represents the fraction of activity which is reversibly poisoned at the end of the first deactivation step.

The second fouling step is characterized by the following relationship:

$$\frac{d\langle a\rangle}{dt} = -kR_0\langle a\rangle. \tag{2}$$

This deactivation step has an activation energy calculated for the rate constant k of 39 kcal/g mole. Total regeneration of catalytic activity is not achievable by a flowing stream of hydrogen under reaction conditions during this step. An activity level equal to $\langle a_{\mathrm{REG}}\rangle$ is obtainable though and is approximated by the expression

$$\langle a_{\mathrm{REG}}\rangle = \frac{\langle a\rangle}{\langle a_{\mathrm{INT}}\rangle}. \tag{3}$$

The addition of Re to an unsulfided Pt catalyst does not affect the initial deactivation period. A Pt–Re catalyst which is deactivated to an activity level less than $\langle a_{\mathrm{INT}}\rangle$ can be partially regenerated in a flowing stream of hydrogen at reaction temperature and pressure, Fig. 3, and the resulting regenerated activity, $\langle a_{\mathrm{REG}}\rangle$, is still approximated by Eq. (3). However, evaluation of $\langle a_{\mathrm{INT}}\rangle$ for a Pt–Re catalyst is complicated by the nonlinear relationship between log $\langle a\rangle$

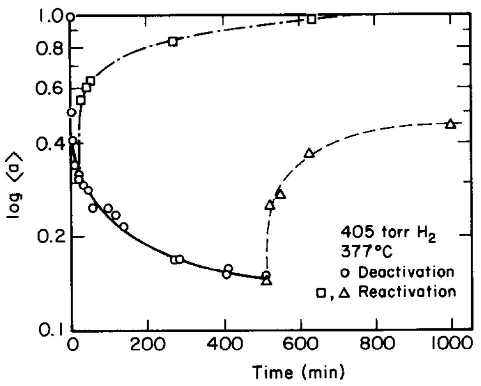


FIG. 3. Deactivation–hydrogen reactivation of a Pt–Re catalyst.

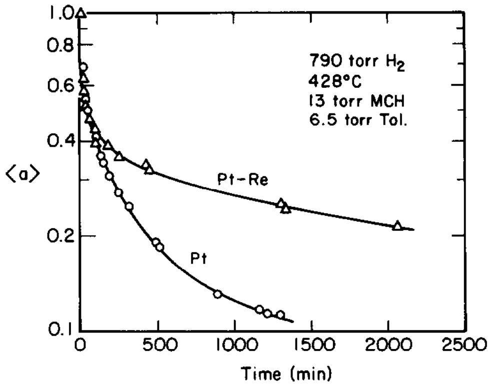


FIG. 5. MCH deactivation characteristics; elevated temperature and hydrogen pressure.

and time for this bimetallic catalyst during the slow-deactivation-rate period. It can be easily obtained though from Pt catalyst results where log ⟨*a*⟩ varies linearly with time during the slow-deactivation-rate period and applied directly to the Pt–Re case.

The addition of Re to a Pt catalyst affects the second deactivation step, Figs. 4 and 5. For a Pt–Re catalyst the rate of deactivation during the second deactivation step is reduced and is no longer proportional to reaction rate. Results presented in Fig. 5 are for experiments conducted at an elevated temperature and hydrogen pressure. The system temperature is increased in order to compensate for the reduced deactivation rates observed for the Pt–Re catalyst during the second deactivation period while the system hydrogen pressure is increased so as to minimize the extent of the common initial deactivation period observed between a Pt and a Pt–Re catalyst. The same relative trends between a Pt and a Pt–Re catalyst shown in Fig. 4 are recognized in Fig. 5. These trends are: little if any difference in initial deactivation characteristics and reduced deactivation rates for a Pt–Re catalyst during the long-term deactivation period. Under these elevated reaction conditions there is a change in the long-term deactivation characteristics of a Pt catalyst; that is, no longer is there a linear relationship between log *a* and time which is displayed under less severe reaction conditions.

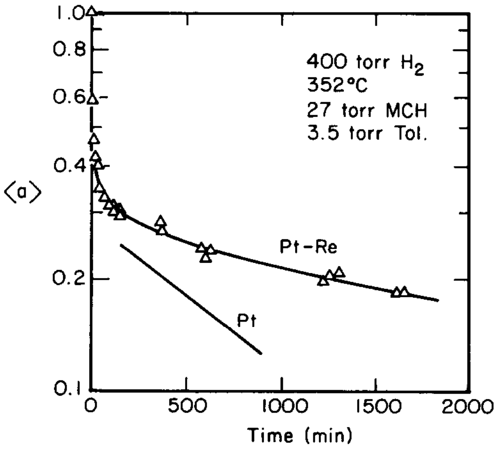


FIG. 4. MCH deactivation characteristics; low temperature and hydrogen pressure.

Deactivation characteristics for presulfided Pt and Pt–Re catalysts are presented in Fig. 6. Reaction conditions employed in this study are approximately equal to those used in the unsulfided study presented in Fig. 5. The Pt and Pt–Re catalytic activities plotted in Fig. 6 are based on respective initial MCH dehydrogenation reaction rates observed for unsulfided catalyst. Because of this, activities plotted in the sulfided study, Fig. 6, can be compared directly to those of the unsulfided study, Fig. 5. The decreased initial activities plotted in Fig. 6 are in agreement with the presulfiding experiments presented in Fig. 2.

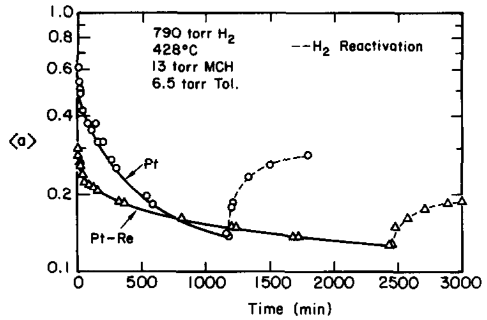


FIG. 6. Sulfided MCH deactivation characteristics; elevated temperature and hydrogen pressure.

The fouling characteristics for a Pt catalyst are not greatly affected by a sulfidation pretreatment step. This is not the case for a Pt–Re catalyst. As shown in Fig. 6 for a Pt–Re catalyst, presulfiding results in a reduction of the deactivation rates during both the initial and long-term deactivation periods; also, it reduces the degree of reversibility of a deactivated catalyst. Reversibility is measured by the extent of recovery during the hydrogen reactivation period and as depicted in Fig. 6, the sulfided Pt–Re catalyst does not reactivate as readily as the sulfided Pt catalyst.

Dealkylation selectivities, S_{DA}, are presented in Table 1 for the four cases presented in Figs. 5 and 6. Selectivity is measured by the ratio of the benzene production rate to the combined benzene plus toluene production rate. For either catalyst the deactivation rate for the dealkylation reaction is greater than the deactivation rate for the dehydrogenation reaction. Carbon–carbon bond-breaking reactions over a metal catalyst are usually structure sensitive and the coking process is known to have a larger effect on structure-sensitive reactions (*23*). This is in agreement with the trend in selectivities tabulated in Table 1.

Acidic Site Probe—MCP Initial Rate Kinetics

The dehydroisomerization of MCP to benzene is equally catalyzed by either a Pt or Pt–Re catalyst. Both sulfided and unsulfided catalysts were studied at 475°C, 730 Torr hydrogen, and 70 Torr MCP. Nominally the conversion of MCP to benzene is less than 20%. MCP dehydroisomerization reaction rates exhibit slightly negative MCP kinetics. For example, under nominal reaction conditions, 0.007 mole of benzene per hour per gram of catalyst was produced. Reducing MCP concentration to one-fourth its nominal value results in an increase in reaction rate to 0.0091 mole per hour per gram of catalyst. Observed reaction rates are in agreement with those published by Sinfelt and Rohrer (*25*).

Though these catalysts equally catalyze the dehydroisomerization of MCP, the ring-opening activity of a sulfided Pt–Re catalyst is less than half that of an unsulfided or sulfided Pt catalyst. This result agrees with the observation of Menon and Prasad (*12*). Ring opening is the significant secondary reaction accompanying dehydroisomerization and yields 2-methylpentane, 3-methylpentane, and normal hexane. From the combined products of both isohexanes, normal hexane and benzene, the selectivity for the initial production of benzene is approximately 70% for a Pt catalyst under the nominal reaction conditions. This result agrees with the findings of Sinfelt and Rohrer (*25*) at 2 atm hydrogen partial pressure, 0.1 atm MCP partial pressure, and 471°C.

The initial distribution of secondary products from either a sulfided or unsulfided catalyst is roughly in the proportion of 2, 1, and 2 parts for 2-methylpentane, 3-

TABLE 1

The Dependence of Dealkylation Selectivity on Catalyst Type

	S_{DA}		
	0 min	20 min	60 min
Pt	0.069	0.043	0.031
Pt–Re	0.021	0.015	0.014
Presulfided Pt	0.045	0.017	0.014
Presulfided Pt–Re	0.018	0.005	0.005

methylpentane, and normal hexane, respectively. Secondary products from the dehydroisomerization of MCP rich in 2-methylpentane were observed by Smith *et al.* (*20*) when the alumina support was poisoned with *n*-propylamine leaving only active metallic sites. Dartigues *et al.* (*28*), in their investigation of the structure sensitivity for the ring opening of MCP, found an equal probability of breaking all five cyclic carbon–carbon bonds for a highly dispersed Pt-on-alumina catalyst. Similarly, deJongste *et al.* (*36*) found that a Cu-rich Pt–Cu catalyst supported on silica also gave nonselective ring opening of MCP. Ring opening of MCP catalyzed by γ-alumina yields predominantly normal hexane (*20*). This suggests that the highly dispersed metal function of a Pt or Pt–Re catalyst is responsible for the ring-opening activity of these catalysts.

Rhenium, though a very strong paraffin hydrogenolysis catalyst, is not that active in opening the cyclopentane ring. Betizeau *et al.* (*11*) report that Pt is 3.3 times as active as Re in the hydrogenolysis of cyclopentane at 240°C. In addition, they report that the energy of activation for the hydrogenolysis of cyclopentane over Pt and Re is 35 and 12 kcal/g mole, respectively. Due to the large difference in activation energies, bulk Re should contribute little to the catalytic activity of a Pt–Re catalyst at 475°C. Indeed, the work of Menon and Prasad (*12*) and our results indicate a slight reduction in the ring-opening activity of a nonsulfided Pt–Re catalyst over a nonsulfided Pt catalyst.

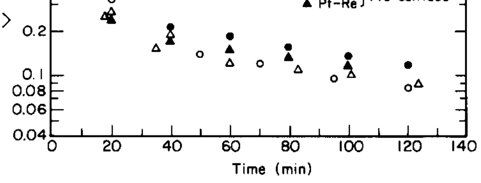


FIG. 7. MCP deactivation characteristics.

Fouling by MCP Dehydroisomerization

The fouling characteristics of a Pt and a Pt–Re catalyst are shown in Fig. 7. Results for both presulfided and unsulfided catalysts are presented. Catalytic activity is measured as the ratio of benzene production rate, $\mathcal{R}$, to initial benzene production rate, $\mathcal{R}_0$. Little, if any, difference is observed in the fouling characteristics of a Pt catalyst on the addition of Re. In addition, presulfiding either a Pt or a Pt–Re catalyst before use has little effect in abating the fouling under these severe reaction conditions.

Decreased activities with respect to time shown in Fig. 7 are attributable to a reduction in the ability of the acidic function to catalyze the ring enlargement of MCP^{2-} to cyclohexene. This indicates that the addition of Re to a Pt reforming catalyst does not directly alter the characteristics of the support to ring enlargement provided that sufficient metallic activity remains during the deactivation experiment to supply an ample production of MCP^{2-}. Sinfelt and Rohrer (*25*) have noted that at low hydrogen partial pressure extensive fouling of the metallic sites does occur, and under these conditions the number of active metallic sites can be reduced to a level where the dehydrogenation of MCP to MCP^{2-} may become the controlling step. Though the yield of MCH^{2-} did drop during the time span of a deactivation experiment, the severity is far less than the decrease in observed benzene production. The effect of changes in MCP^{2-} concentration on the production of benzene should be minimal because of the observed near-zero-order kinetic effect of MCP concentration, and subsequently MCP^{2-} concentration, on initial benzene production rates.

CONCLUSIONS

The addition of Re to a chlorinated Pt reforming catalyst has a marked effect on the metallic function but not the acidic function of this catalyst for the model reactions tested. However, this does not preclude an effect of added rhenium on the acidic function of the catalyst for other support reactions.

Postulated models devised to explain how Re changes the metallic function of a Pt reforming catalyst must be consistent with the following observations:

1. minor change in observed initial MCH dehydrogenation reaction rates for nonsulfided catalysts;
2. decrease in dealkylation reaction rates;
3. decrease in MCP ring-opening reaction rates for a presulfided catalyst;
4. increased sensitivity of initial MCH reaction rates to hydrogen sulfide;
5. minor change in the initial MCH fouling period for an unsulfided catalyst;
6. marked reduction in the rate of deactivation during the long-term MCH deactivation experiments;
7. changes in both the initial and long-term MCH fouling characteristics of a presulfided catalyst.

Approximately equal metallic Pt surface areas for the Pt and Pt–Re catalysts could explain the small change in dehydrogenation reaction rates observed for the MCH reaction which demonstrates modest structure sensitivity. Alloying the metallic Pt sites with Re or a reduction in metallic particle size can explain the reduced dealkylation and ring-opening reaction rates of a Pt–Re catalyst since both these reactions are structure sensitive, and alloys are known to affect structure-sensitive reactions (*37, 38*). This same argument can be applied to the temperature-sensitive long-term deactivation period as reduced deactivation rates have been observed for catalysts with smaller metallic particle sizes (*32*) or by alloying (*37*). The increased sensitivity demonstrated by reactions catalyzed by the metallic function of a Pt–Re catalyst to a hydrogen sulfide pretreatment step points to a strong interaction between Pt and sulfur, which could result from an alloy between Pt and Re with Re having a strong affinity for sulfur. The presence of alloyed Pt–Re (bimetallic clusters) would model the observed behavior of the metallic function of this Pt–Re catalyst.

More direct evidence of an interaction between Pt and Re on similar catalysts has been obtained using temperature-programmed reductions, hydrogen chemisorption, and metal titrations (*39*). This work demonstrates that Pt and Re on this catalyst do not behave as the sum of the individual components but suggests a bimetallic cluster, alloy, or an interaction through a support modification.

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