JOURNAL OF CATALYSIS 88, 163–176 (1984)

Activity, Yield Patterns, and Coking Behavior of Pt and PtRe Catalysts during Dehydrogenation of Methylcyclohexane

II. Influence of Sulfur

ROBERT W. COUGHLIN, AKRAM HASAN, AND K. KAWAKAMI[1]

Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut 06268

Received August 15, 1983; revised January 27, 1984

The presence of small amounts of sulfur lowers hydrocracking activity for both Pt and PtRe catalysts. Treatment of coked PtRe in pure H_2 restores substantial hydrogenolysis activity when sulfur is absent, but in the presence of sulfur such activity appears to be irreversibly poisoned. Hydrogenolysis activity of coked Pt catalysts is not restored by hydrogen treatment regardless of the presence of sulfur. Sulfur retards deactivation of the dehydroaromatization activity of PtRe catalysts more significantly than it does for monometallic Pt catalysts. Presulfiding PtRe catalyst with H_2S was more effective than merely adding thiophene to the feed. The greatest enhancement in aromatics yield was obtained with H_2S-presulfided PtRe when thiophene was also in the hydrocarbon feed. Excessive amounts of S deactivated the dehydroaromatization activities of both catalysts but the effect was far more pronounced with PtRe. Gravimetric measurements show that coke deposition on PtRe catalysts is greatly retarded by S and such diminution of coke deposition is closely associated with the retarded rates of deactivation of these catalysts. The observations are generally in accord with a model that includes the following major features: (1) hydrogenolysis at kinked terrace edges of metal crystallites, (2) dehydroaromatization by the concerted action of exposed metal atoms in the terraces together with a disordered carbonaceous overlayer, (3) rearrangement of this disordered layer to a noncatalytic graphitic deposit, (4) deactivation of hydrogenolysis (kinked edge) sites by either sulfur or carbon, especially by sulfur when Re is present, and (5) retardation of the growth and 3-dimensional rearrangement of the carbonaceous overlayer by sulfur bound to Re atoms in the surfaces of the crystallite terraces.

INTRODUCTION

Since the introduction of platinum as a reforming catalyst, it has been recognized that the presence of sulfur compounds in the feed can gradually poison the catalyst. Sulfur is a commonly encountered impurity and many of its bivalent compounds can readily react with and block Pt atoms of the catalyst. Because this can cause a complete loss of activity (*1*), sulfur concentrations must be kept below about 1 ppm in the feed to freshly charged catalyst (*2*). PtRe catalysts are also known to be sensitive to sulfur and sulfur concentrations less than about 1 ppm have been specified for these catalysts (*3, 4*).

As is often the case in catalysis, sulfur is not totally unwanted. A low concentration of sulfur in the feed or in a pretreatment gas can favorably reduce excessively high catalytic activities of Pt and PtRe catalysts which can cause unwanted exothermic hydrocracking. For example, a recent patent granted to Antos (*5*) discloses a method claimed to selectively sulfide the Re atoms but not the Pt atoms in a bimetallic reforming catalyst. In this way, the controlled addition of sulfur to the catalyst was found to improve the C_{5+} yield and yield stability during reforming. Demethylation and other hydrogenolysis reactions were also decreased significantly by selectively sulfiding the catalyst.

---

[1] Present address: Kyushu University, Fukuoka 812, Japan.

0021-9517/84 $3.00

Evidence with bimetallic alloy catalysts that large Pt or Ni ensembles are required for hydrogenolysis has been reported in several instances by Sachtler, Sinfelt, and co-workers (*14*, *22–24*). Ensembles of contiguous Pt (or Ni) atoms are required for hydrogenoloysis and subsequent transformation of the cracked products into carbonaceous deposits. Alloying reduces the concentration of large ensembles and the formation of "coke" deposits is thereby reduced. Biloen and co-workers (*6*) have reported that the combined action of Re and S produced a Pt catalyst very selective for mild dehydrogenation. They used low concentrations of hydrogen sulfide in hydrogen (5 ppm) to selectively presulfide the Re atoms rather than the Pt atoms in a PtRe catalyst. We show below that this combination of Re and S is extremely effective for reducing carbon deposition.

Although it is generally recognized that Re prolongs the active lifetime of Pt-reforming catalyst and that there appears to be a synergistic interaction of Pt, Re, S, and carbonaceous deposits, such behavior is poorly understood. Recent work by Somorjai and co-workers (*9*, *15*, *16*) has shed considerable light on phenomena involving carbonaceous deposits on single crystals of Pt, but the roles of Re and S have not yet been so well scrutinized. Perhaps Haensel (*17*) was the first to report that sulfur in the feed stabilizes catalytic activity during naphtha reforming. More recently work by Menon *et al.* (*18*) has shown that hydrogenolysis activity of a Pt catalyst was reduced to zero only when the atomic ratio of S per exposed Pt atom was about unity, that a fresh catalyst and one having only irreversibly adsorbed sulfur had about the same activity and selectivity for reforming reactions of *n*-hexane and that hydrogenolysis was suppressed and isomerization and aromatization enhanced only by reversibly adsorbed S beyond that held irreversibly. For a PtRe catalyst, however, reversibly adsorbed S alone can suppress hydrocracking (*19*). The present paper presents results of experiments made to learn the effects of sulfiding Pt and PtRe catalysts on product yields and the formation of carbonaceous deposits using methylcyclohexane (MCH) as a model compound.

The experimental results reported below are discussed in terms of the viewpoint (*6*, *14*, *22–24*) of ensembles as hydrogenolysis sites as well as the viewpoint that edge-kinks (*9*, *15*, *16*) serve as hydrogenolysis sites. These viewpoints are not necessarily inconsistent and it may be possible to synthesize them as suggested near the end of this paper. Of course the concepts of edges and terraces on high-index surfaces of large crystals may not be at all realistic for the very tiny crystals of the highly dispersed metal catalysts studied here. It might here be better, therefore, to speak of high- or low-coordination-number sites instead of terraces or kinks. We retain, however, the more convenient terms: terraces and kinks.

EXPERIMENTAL

The catalysts employed were those described in Table 1 of the accompanying paper (*7*) as "Lot-2." Experiments were done in the same way, aside from sulfiding which was done by adding thiophene (10–75 ppm) to the MCH feed or by presulfiding the catalysts with hydrogen sulfide (10 ppm) in hydrogen. In order to presulfide selectively only Re atoms which have a well-established affinity for sulfur (*5*, *6*), low concentrations of hydrogen sulfide in hydrogen (10 ppm) were used. This gas mixture was prepared by diluting a Matheson analyzed preparation of 60 ppm H_2S in H_2. Hydrogen sulfide pretreatment periods from 26 to 50 h correspond to S/Re atomic ratios of 0.75–1.5, assuming that the hydrogen sulfide adsorbs completely, and exclusively on the Re atoms. For comparison, monometallic Pt catalysts were similarly presulfided.

Kitagawa detector tubes purchased from Matheson (limit of detection 0.3 ppm, range 0.75–150 ppm) were used to measure H_2S concentration in the sulfiding feed gas, in the pretreatment effluent gas, in the reaction effluent gas during hydrocarbon reaction, and in the effluent gas during treatment of used catalysts with pure hydrogen.

Coke deposition during catalytic hydrocarbon reaction and coke removal during treatment in pure hydrogen was monitored by continuous weighing of a catalyst sample (100 mg) exposed to the appropriate continuously flowing gas in a Cahn electrobalance.

The experiments with MCH reported here accomplished aromatization through mere dehydrogenation. On the other hand, with other compounds of interest (e.g., *n*-paraffins) aromatization involves ring closure as the slow step and dehydrogenation does not count as a rate-determining step contributing to total conversion. Thus statements and conclusions in the present case as to activity maintenance will not necessarily hold, and are likely to differ, in the practical cases where the most important reactions involve changes in the carbon skeleton. Accordingly, caution should be exercised when comparing the present data with those for naphtha conversion.

Some checking of cracked (C_5-)products was done for the sulfided catalysts; they were mainly C_1 and C_2 compounds; no significant C_5 compounds were detected.

PROCEDURE

The catalyst temperature was slowly raised to 500°C in flowing air. Pretreatment included exposure to dry air (50 ml/min) for 1 h followed by flowing hydrogen (50 ml/min) for 3 h keeping the temperature constant at 500°C. Sulfiding with H_2S was done after reduction in hydrogen. The experimental procedure involved cyclic exposure of the fresh or sulfided catalysts to hydrocarbon feed (50 ml/min) for 20 h followed by hydrogenation using pure hydrogen (50 ml/min) for 5 h. This cycle was repeated for both the Pt and PtRe catalysts with various periods of exposure to hydrocarbon and hydrogen. Concentrations of methylcyclohexane, methylcyclohexenes, benzene, and toluene in the product were measured periodically by gas chromatography using a $\frac{1}{8}$-in., stainless-steel column containing 10 wt% Carbowax 20 M on 80/100 mesh Supelcoport, maintained at 80°C. Further experimental details are given elsewhere (*8*).

RESULTS AND DISCUSSION

A. Experiments with Thiophene

The conversion of MCH over Pt and PtRe catalysts is very high with 10 ppm thiophene present in the MCH feed. After 20 h MCH conversion over PtRe is greater than 99% and over Pt greater than 96%. Thus, for either catalyst, the fall in conversion is much less severe with thiophene in the feed compared to the previously reported (*7*) sulfur-free feed. Upon subsequent hydrogen treatment, both catalysts recover some lost activity; moreover, the platinum catalyst shows greater recovery in the thiophene case. However, as coke redeposits on the two catalysts ($t = 25$ to 32 h) the activity of the Pt catalyst drops again at a faster rate than the PtRe catalyst during this second reaction cycle. The second H_2 treatment and MCH reaction cycle causes conversions similar to those seen in the first cycle.

During cyclic exposure to MCH + thiophene (10 ppm) followed by pure hydrogen, the PtRe catalyst also exhibits a pattern of individual product yields as a function of time that is significantly different than that observed with monometallic Pt. This is evident from a comparison of Fig. 1 (PtRe catalyst) with Fig. 2 (Pt catalyst). During the first 20 h of exposure to thiophene-containing MCH feed, toluene yield rises at a faster rate with the Pt catalyst than with the PtRe catalyst. Moreover, with the Pt catalyst the toluene yield remains high throughout this 20-h period in the presence of thiophene. This persistence of toluene yield can be attributed to the presence of the thiophene in view of our observation reported in the accompanying paper (*7*) that in the case of sulfur-free MCH feed the toluene yield rises to a peak and then falls. A possible hypothesis is that thiophene poisons spe-

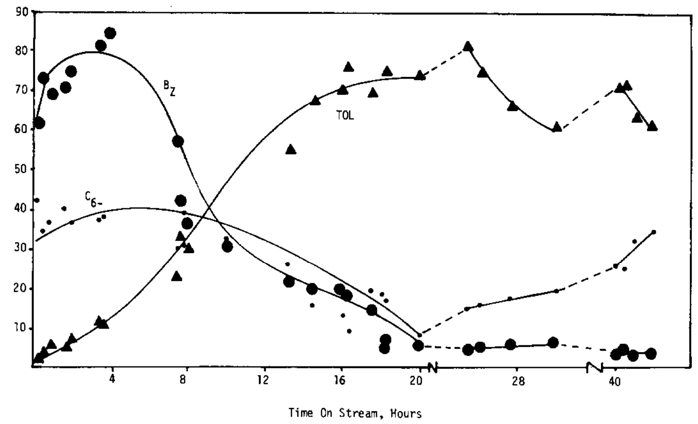


FIG. 1. Activity pattern of product yields at 500°C over PtRe catalyst with 10 ppm thiophene in the MCH feed. (▲) Toluene yield, (●) benzene yield, (•) C_6-yield. Solid line: hydrocarbon feed, H_2/MCH = 9 (molar ratio) with 10 ppm thiophene, dashed line: pure hydrogen.

cific sites such as the kinks in the atomic steps of the platinum surface shown (9) to be hydrogenolysis sites. As this poisoning effect grows (more sulfur deposited in addition to coke) the Pt catalyst would become more selective for toluene. The effect of thiophene on the benzene yield for both catalysts is similar initially: that is, an initial increase in benzene yield when thiophene is present. For the Pt catalyst, however, the benzene yield then falls more rapidly. The toluene yield for the PtRe catalyst, in the presence of thiophene, is very low initially but then increases steadily and eventually surpasses that of the Pt catalyst after 16 h of exposure. For the Pt catalyst it appears that the sulfur effectively poisons hydrogenolysis sites as does coke deposition so that the two effects combine in an additive way. For PtRe, however, the combined action of S and Re, as shown below by microbalance experiments, suppresses and greatly delays coke deposition. This behavior is entirely different than in the case of monometallic Pt and the result is a much slower rise in selectivity for toluene formation in parallel with coke deposition.

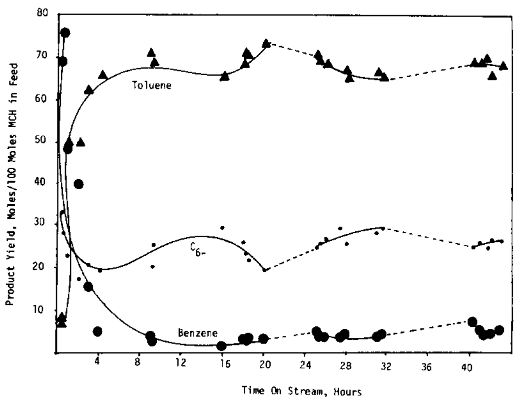


FIG. 2. Activity pattern of product yields at 500°C over Pt catalyst with 10 ppm thiophene in the MCH feed. Symbols and conditions as in Fig. 1.

It is interesting to note that after about 8 h of exposure, the amount of cracked C_6-products and benzene were about equal and followed similar trends in the case of PtRe catalyst (Fig. 1). This C_6-fraction consisted mainly of methane (about 95%), so it appears that the PtRe catalyst becomes very selective with two main reactions on the surface: MCH dehydrogenation to toluene and demethylation to form benzene and methane. For the Pt catalysts different behavior may be associated with cracked products other than methane formed, presumably, by other routes.

After 20 h of exposure to MCH, treatment with pure hydrogen for 5 h produced an increased toluene yield for the PtRe catalyst (Fig. 1) and a slight decrease for the Pt catalyst (Fig. 2). As for benzene and cracked product yields, the hydrogen treatment produced a similar effect for the two catalysts: a slight increase in C_6-yield and almost no effect on benzene yield. A possible interpretation of this behavior is that Re catalyzes the selective removal of S from dehydrogenation sites but that the hydrogenolysis sites are poisoned irreversibly by S in the case of RePt catalysts. This agrees well with the findings of Menon and Prasad (*19*) that early, irreversible S poisoning of PtRe catalysts was sufficient to inhibit hydrogenolysis of *n*-hexane or methylcyclopentane. As shown in the accompanying paper (*7*), hydrogen treatment of coked but S-free PtRe catalysts restores hydrogenolysis activity, perhaps by removing carbon from the respective ensemble or kink sites or by changing the surface concentration of PtRe ensembles. This restoration of the hydrogenolytic activity of S-free PtRe catalysts is markedly and dramatically different than the behavior of PtRe catalysts when thiophene is in the feed or after presulfiding (see below).

Hydrogen treatment of the coked PtRe catalyst has different effects depending on whether or not there is thiophene in the feed. Comparing Fig. 1 (thiophene) with Fig. 3 of the previous paper (*7*) (no thiophene) suggests that thiophene changes the pattern of coke deposition on PtRe and that subsequent exposure to hydrogen is less effective for regenerating hydrocracking sites which are probably poisoned by sulfur. If, as has been suggested, kinks (*7, 9*) at terrace edges or ensembles (*6, 14, 22–24*) on the metal surface are selective for hydrogenolysis, then it appears that thiophene or S from thiophene may adsorb strongly on these ensemble or kink sites and not be removed by hydrogen but may be removed from dehydrogenation sites by treatment in pure hydrogen. Somorjai (*9*) also pointed out that such kinks on the Pt surface have strong chemical bonding ability in agreement with the present interpretation; Re atoms in the surfaces of alloy catalysts also bonds sulfur strongly. As the accompany ing paper shows (*7*), hydrogen treatment causes an abrupt initial increase in cracking activity of coked but sulfur-free PtRe which had been exposed previously to sulfur-free MCH. It appears, therefore, that thiophene in the feed may selectively poison these metal cracking sites in a form not easily removed by hydrogen treatment. During subsequent hydrogen treatment traces of hydrogen sulfide were detected leaving the catalyst bed which suggests that thiophene decomposition may leave atomic sulfur on the surface.

In general, the cracking activity of either Pt or PtRe catalysts was retarded by low concentrations (10–25 ppm) of thiophene in the feed, and this suggests thiophene may selectively poison the kinks in the atomic steps or ensembles of Pt in the terraces. In the case of the sulfur-free bimetallic PtRe catalyst it appears that carbon deactivation of the hydrocracking sites (perhaps kinks, perhaps surface-concentrations of ensembles) can be substantially reversed by hydrogen treatment as shown in the accompanying paper (*7*). However, sulfur deactivation of these sites cannot be so reversed to a significant extent as shown here. If we presume that the crystallites of monometallic Pt and bimetallic PtRe catalysts have such hydrocracking sites (kinks or ensembles) in each case, then it can be argued that hydrogen treatment may restore carbon-poisoned sites more easily than sulfur-poisoned sites.

Increasing thiophene concentration in the feed to 25 ppm produced little additional effect. At 75 ppm however the thiophene drastically reduced the catalytic activity of PtRe but had little additional effect on the performance of the Pt catalyst as is shown in Fig. 3. The PtRe catalyst gets poisoned severely as evident by the sharp fall in MCH conversion to about 60% after 20 h. After hydrogenation (t = 20 to 25 h), the PtRe catalyst recovers some of the lost activity, but further exposure to MCH with 75 ppm thiophene (t = 25 to 32 h) leads to a

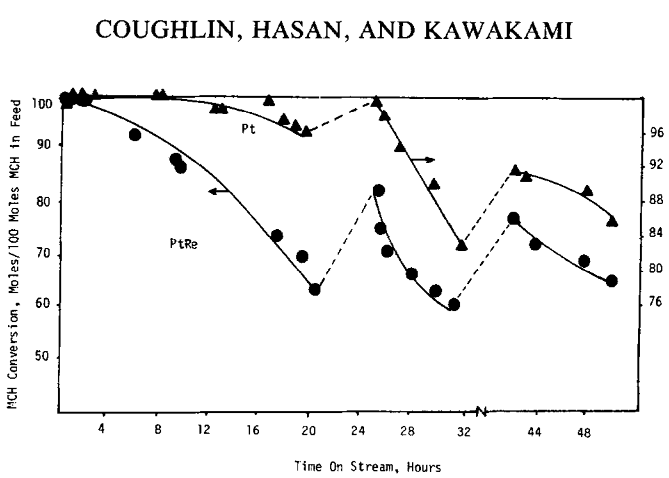


FIG. 3. Activity pattern of MCH conversion at 500°C over Pt and Pt/Re catalysts with 75 ppm thiophene in feed; dashed line: pure H_2.

repetition of the trend of the first 20 h. This trend repeats during subsequent cycles of exposure to MCH and treatment in pure hydrogen. The Pt catalyst, on the other hand, is more stable and seems to have better tolerance to such high thiophene concentrations as evident in Fig. 3 where about 94% MCH conversion is still evident after 20 h. A possible explanation of this behavior might involve cracking of thiophene on the Re sites to form atomic sulfur which can poison dehydroaromatization sites. Another hypothesis is that when the chemical potential of S become sufficiently large to sulfide all Re in terraces of the bimetallic crystal this causes a very effective poisoning of ensemble terrace sites for aromatization. This poisoning might be due to adsorption of intact thiophene molecules at Re atoms in the terraces whereas such molecules would crack at the kink sites leaving behind S at the kinks.

Figures 4 and 5 show product yields with 75 ppm thiophene as a function of on-stream time for the Pt and PtRe catalyst, respectively. The performance of the Pt catalyst in the presence of 75 ppm thiophene (Fig. 4) is very similar to its performance with 10 ppm thiophene (Fig. 2). For the PtRe catalyst, however, the higher thiophene concentration is associated with decreased toluene yield as a comparison of Figs. 5 and 1 (10 ppm thiophene) reveals. It is also evident that, although the toluene yields are substantially lower, the general pattern was not greatly affected by the higher sulfur concentration.

In summary, a low concentration of thio-

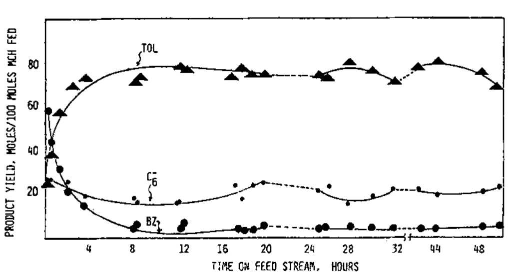


FIG. 4. Activity pattern of product yields at 500°C over Pt catalyst with 75 ppm thiophene in feed; dashed line: pure H_2.

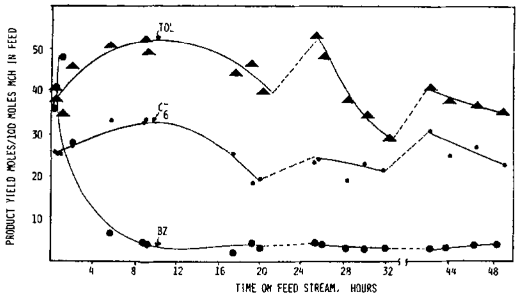


FIG. 5. Activity pattern of product yields at 500°C over PtRe catalyst with 75 ppm thiophene in feed; dashed line: pure H_2.

phene added to the MCH feed, up to about 25 ppm, had a minor effect on the performance of either Pt or PtRe catalysts after they stabilize (about 6 h on stream). Moreover, such an addition may be beneficial for either Pt or PtRe catalyst only after several hours on stream. However, the present results also indicate that higher concentration of thiophene (75 ppm) in the feed HC causes severe poisoning of PtRe catalytic activity (Figs. 3 and 5) but causes little further change in the activity of a Pt catalyst (Figs. 3 and 4) which is already poisoned at lower thiophene concentration. The results for thiophene poisoning may be influenced by unhomogeneous deposition of sulfur at the front end of the reactor, especially at early times and for low thiophene concentrations. With 75 ppm thiophene, the results may be more reflective of homogeneous poisoning. The next results to be discussed were obtained after presulfiding and, therefore, probably with a more homogeneous distribution of sulfur in the reactor during the early hours of the experiments.

B. Experiments with Presulfided Catalysts

Figure 6 compares the conversion of MCH over presulfided Pt and PtRe catalysts as a function of on-stream time. Both catalysts were presulfided about 26 h in a hydrogen stream containing 10 ppm hydrogen sulfide to produce the atomic ratios S/Pt = 0.75 for the Pt catalyst and S/Re = 0.75 for the PtRe catalyst. Amounts of sulfur were computed by mass balance assuming all the sulfur from the gas stream deposited on the catalyst. Most of the sulfur may be assumed to adsorb on Re when Re is present in the catalyst as suggested by Antos (*5*) and Biloen and co-workers (*6*). Moreover Kelley *et al.* (*20*) have reported results of ion-scattering experiments which show that sulfur is most strongly associated with Re on PtRe/Al_2O_3 catalysts. In the present work, pretreatment of the PtRe catalyst with 10 ppm hydrogen sulfide in hydrogen for about 26 h transformed it into a very stable catalyst which did not lose MCH conversion activity over long periods of time. In fact, after 20 h of exposure the conversion of MCH over this presulfided PtRe catalyst remained at nearly 100% and, for this reason the MCH feed was continued for 12 additional hours with no intervening treatment in pure hydrogen. Microbalance experiments reported below show that presulfiding a PtRe catalyst substantially suppresses the deposition of carbonaceous deposits, unlike the case of monometallic Pt for which such deposit formation is always greater. Although presulfiding sup-

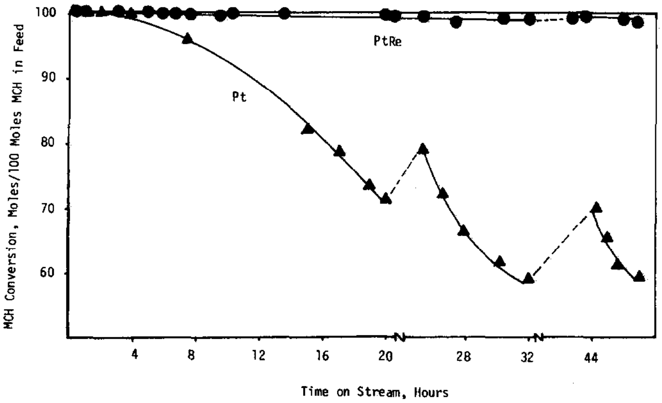


FIG. 6. Conversion activity over presulfided Pt and PtRe catalysts. Sulfiding time = 26, $T = 500°C$. S/Pt = 0.75 (atomic) for Pt catalyst, S/Re = 0.75 (atomic) for Re catalyst, (▲) 0.35% Pt, 0.97% Cl/Al_2O_3, (●) 0.36% Pt, 0.36% Re, 1.07% Cl/Al_2O_3. Solid line: H_2/MCH = 9 molar ratio, dashed line: pure hydrogen.

presses coke formation on Pt catalysts during the first few hours on stream, after about 10 to 15 h there is no longer any great difference in the amount of coke accumulated on presulfided and nonpresulfided Pt catalysts. In contrast, presulfided PtRe catalysts remain largely free of coke even beyond 20 h of exposure to the MCH feed. Thus the maintenance of high, gross, overall conversion activity of the presulfided PtRe catalyst over a period exceeding 20 h parallels the suppression of carbonaceous deposit formation on the catalyst. This does not mean, however, that the chemical nature of this deposit is unimportant compared to its amount. As shown below, product yields and selectivities did change during this period of suppressed coke formation with presulfided PtRe. The Pt catalyst behaved quite differently. Its initial activity was high, similar to that of an unsulfided Pt or PtRe catalyst. However, after a substantial amount of coke deposited on the Pt catalyst (about 4 h exposure to MCH) the conversion of MCH fell considerably and continuously. Regenerating the presulfided Pt catalyst with hydrogen restored some of its lost activity but the activity fell rapidly again when the MCH feed was switched back on. The data show that the presulfided PtRe catalyst maintained significantly higher MCH conversion throughout the experimental period as compared to an unsulfided PtRe catalyst. In contrast to the behavior of the bimetallic catalyst, the presulfided Pt catalyst behaves about the same as an unsulfided Pt catalyst; i.e., presulfiding the Pt catalyst seems to have little effect on the overall pattern of MCH conversion with time.

Figures 7 and 8 show the product yields from presulfided Pt and PtRe catalysts, respectively, and Fig. 9 compares the yield of total aromatics (benzene + toluene) for the two catalysts. Both presulfided catalysts exhibit high initial yields of toluene and total aromatics. As coke accumulates on the catalysts, however, the yields of toluene and of total aromatics decrease significantly for the presulfided Pt catalyst whereas these yields remain high for the presulfided PtRe catalyst throughout the first 20 h of exposure to MCH. An initial trade-off is evident between benzene yield and toluene yield for the PtRe catalyst. The initial high toluene yields and low benzene yields for both catalysts can be understood in terms of sulfur poisoning of hydrogenolysis sites. This could occur by chemisorption of sulfur at kink sites or by chemisorption of sulfur on surface Re thereby stabilizing such Re which disrupts and deactivates surface ensembles of Pt.

Considering the results of the accompanying paper (*7*) it appears that carbon deposition can poison metal cracking sites. Figure 8 of the present paper shows that 25 h of presulfiding poisoned most of the metal

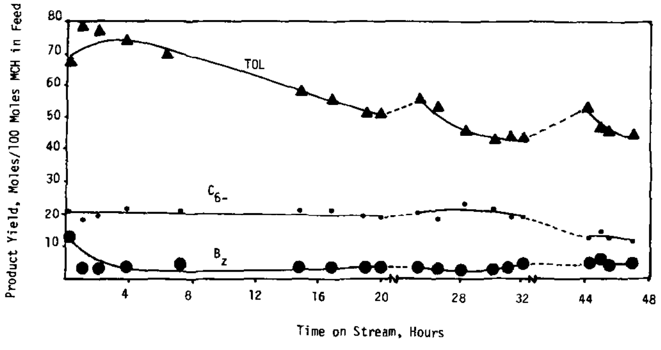


FIG. 7. Product yields at 500°C for presulfided Pt catalyst. Conditions as in Fig. 6. (▲) Toluene yield, (•) C_6-yield, (●) benzene yield. Dashed line: pure H_2.

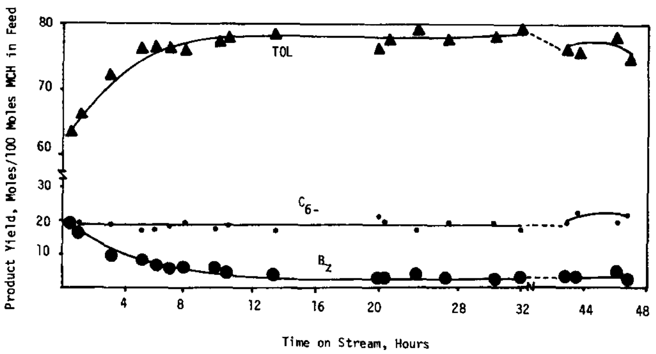


FIG. 8. Product yields at 500°C for presulfided PtRe catalyst. Conditions and symbols as in Fig. 7.

cracking sites of the PtRe catalyst. If it is assumed that, during subsequent exposure of this presulfided catalyst to MCH, coke deposits tend to deactivate the remaining cracking sites, then this would account for the increase in toluene and corresponding decrease in benzene yield during the first 4 h. Coke which deposits after this seems to have had no further effect on these sites because it caused no change in yields of toluene or of C_6-cracked products. The persistence of some cracking sites may be associated with unpoisoned acidic sites or with the ability of Re to selectively remove coke precursors (by hydrogenation), or it may be associated with some removal of sulfur from metallic cracking sites. The last-mentioned phenomenon is suggested by the fact that small amounts of H_2S were detected in the products while H_2S-free MCH was fed to the reactor containing presulfided catalyst. Hydrogenation of the PtRe catalyst in the period t = 32 to 42 hours removed some of the coke and some adsorbed sulfur atoms. Figure 8 shows that this hydrogen treatment caused a slight drop in toluene yield and a slight increase in cracked products yield. This suggests that metal cracking sites were reactivated by removing sulfur and coke. Figure 8 also shows that the dehydroaromatization sites were not substantially deactivated during a long period (almost 40 h) of exposure to MCH. A rationalization of this behavior is provided by Sachtler's model (*21*) in which S-capped Re atoms located at the surfaces of the terraces of the metal crystallites (i.e., at the ensemble sites for dehydroaromatiza-

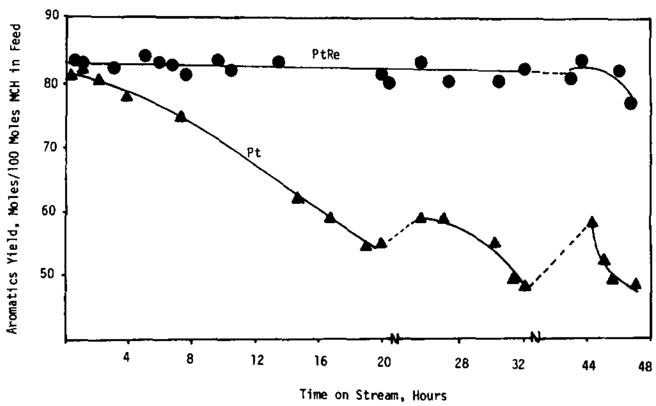


FIG. 9. Aromatics yields over presulfided Pt and PtRe catalysts. Conditions and symbols as in Fig. 6.

tion) interfere with the formation of ordered graphitic overlayers which cause poisoning (*15*).

Figure 7 shows that presulfided Pt behaves very much like unpresulfided Pt (*7*) in that toluene yields fall substantially after about 8 h of exposure to MCH. As in the case of PtRe (Fig. 8), presulfiding Pt lowers the yield of C_6-cracked products, presumably by blocking ensemble or kink sites. The decreased toluene yields associated with graphite-layer poisoning of the dehydrogenation sites (metal crystallite terraces) of the presulfided Pt catalyst (Fig. 7) are not observed on presulfided PtRe catalysts (Fig. 8). Presulfiding these catalysts may be assumed to prevent formation of a graphitic overlayer on the crystal terraces by the disrupting effect of S-capped Re atoms, according to the Sachtler model (*21*).

In addition to substantially different deactivation behaviors during exposure to MCH, the presulfided Pt and PtRe catalysts also responded differently to hydrogen treatment as shown by Figs. 6 and 9. The toluene yields of the PtRe, already high, were little affected by the hydrogen treatment whereas the toluene yields of the Pt catalyst, which had fallen to low values, were restored slightly by exposure to pure hydrogen. Just as for the unsulfided case, the sulfided Pt deactivates rapidly during exposure to MCH, presumably due to coke deposition. The sulfided PtRe is not so affected. This behavior of the sulfided PtRe is in accord with the substantially smaller amounts of carbon which deposit. Such carbon is presumably selectively located on the crystallites and of a modified chemical nature. Also, hydrogen treatment does not increase undesirable hydrocracking activity of the presulfided PtRe catalyst; the sulfided metal cracking sites are not reactivated easily by hydrogen treatment.

Some experiments were also done with more extensively presulfided catalysts: S/Pt = 1.5 for Pt catalyst and S/Re = 1.5 for PtRe catalyst. This presulfided PtRe catalyst gave high MCH conversion (>99%) and high yields of toluene (>80%) and aromatics (>90%), even after exposure to MCH for 20 h. The Pt catalyst with S/Pt = 1.5 showed no substantially different behavior than when presulfided only to the extent S/Pt = 0.75.

The highest yields of toluene and total aromatic compounds were observed when thiophene-contaminated (10 ppm) MCH was reacted over the highly presulfided (S/Re = 1.5) bimetallic catalyst. As shown in Fig. 10, MCH conversion remained greater than 99% during the first 20 h of this experiment. Presumably the thiophene preserves the effects of the presulfiding on the metal crystallites.

Thus, the presence of a low concentration of thiophene in the feed is desirable, preserves the effects of presulfiding, enhances the favorable effects of deposited carbon on yield and selectivity, and decreases the unfavorable effects of such carbonaceous deposits. Treating this catalyst in hydrogen after 20 h exposure to thiophene-containing MCH had no effect on the benzene yield, but decreased toluene yield and increased the yield of cracked products. This was probably due to removal of

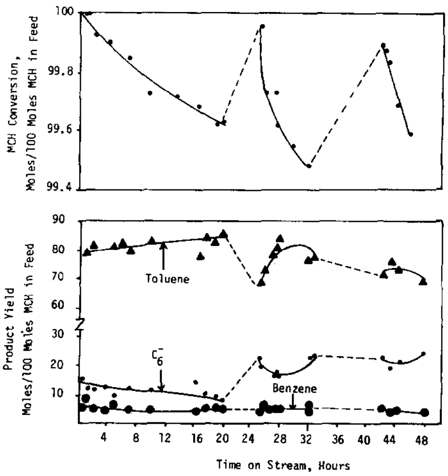


FIG. 10. Yields of toluene and total aromatics over highly sulfided PtRe catalyst with thiophene-contaminated (10 ppm) feed. S/Re = 1.5 atomic ratio. Feed as in Fig. 1. Dashed line: pure H_2 only.

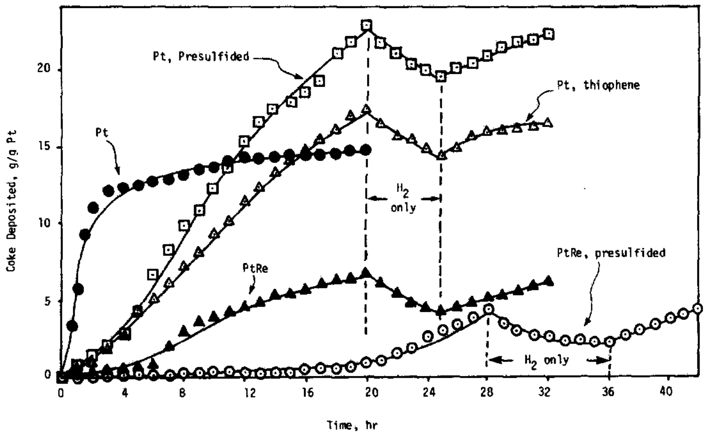


FIG. 11. Gravimetric comparison of coking behavior of sulfided and unsulfided Pt and PtRe catalysts. Feed: H_2/N_2/MCH in molar ratio 9/9/1 WHSV = 3 g MCH/g-cat, h. (●) Pt (0.35% pt, 0.88% Cl/Al_2O_3) initial weight 100.7 mg, (▲) PtRe (0.35% Pt, 0.36% Re, 0.88% Cl/Al_2O_3) initial weight = 92.0 mg, (□) presulfided Pt (as above), S/Pt = 0.75 atomic ratio, initial weight = 96.7 mg, (△) Pt (as above), 10 ppm thiophene in feed, initial weight = 97.5 mg, (○) presulfided PtRe (as above), S/Re = 0.75 atomic ratio, initial weight = 105.4 mg.

sulfur and/or coke which had deactivated cracking sites (kinks).

C. Gravimetric Measurement of Coking

As alluded to above, microbalance experiments were performed in which the catalysts (in some cases presulfided) were continuously weighed to monitor coke deposition during exposure to continuous MCH feed under reaction conditions. The results are given in Fig. 11. Here the behavior of monometallic Pt catalyst is compared under the conditions: A. Presulfided by H_2S; B. Not presulfided but with thiophene in the feed; C. No added sulfur. The behavior of PtRe is shown only for conditions A and C. It is immediately evident that the presence of sulfur (either by presulfiding or by incorporating thiophene in the feed) retards coke deposition on Pt during the early hours of exposure. After about 10–15 h, however, there are no outstanding differences in the gross extent of accumulated coke, although a higher deposition rate appears to persist for the Pt catalyst in the period 10–20 h.

Figure 11 permits a comparison of the behavior of monometallic Pt and PtRe catalysts in the absence of added sulfur. That the presence of Re significantly retards coke deposition is immediately evident. Similar results are shown in the accompanying paper (*7*) but in the present case the catalysts were from a different lot and a different apparatus was employed [Cahn Electrobalance vs the DuPont TGA].

A dramatic suppression of coke deposition is evident in Fig. 11 for presulfided PtRe in comparison with presulfided monometallic Pt. Significantly more coke deposits and accumulates more rapidly on the latter catalyst, whereas the presulfided PtRe catalyst remains almost free of detectable coke during the first 20 h of exposure to the MCH feed. Figure 11 also compares the coking behaviors of PtRe in the presulfided and nonpresulfided state. The dramatic suppression of coke formation by presulfiding PtRe is far greater than the suppression caused by presulfiding monometallic Pt.

The results presented here are in general agreement with the observations of Pfefferle (*10*) that traces of sulfur in naphtha lower the aging rate of a Pt catalyst. Hayes and co-workers (*11*) also showed that coke

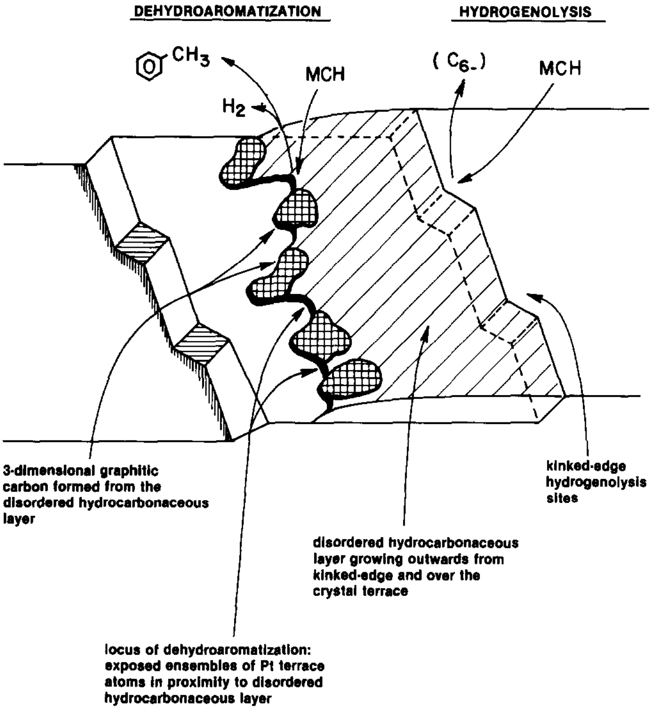


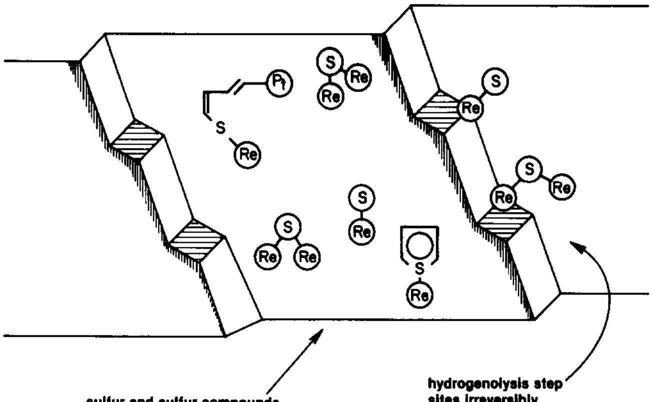
FIG. 12. Schematic diagram of terraced metal-crystallite surface showing coke deposit in absence of sulfur.

deposition was much diminished when Pt catalysts were sulfided. Weisz (*13*) reported that H_2S selectively poisoned hydrogenolysis sites on Pt. Other workers (*12*, *6*) have also shown that sulfur plays an important role with bimetallic PtRe catalysts. The present results are in accord with these viewpoints and further indicate that hydrogenolysis sites can be poisoned by either sulfur or carbon, perhaps competitively. Prepoisoning by sulfur is preferrable, however, in that this then suppresses carbon deposition and possibly rearrangement of disordered carbon to graphitic layers which may tend to deactivate desirable dehydroaromatization sites. It seems likely that in the case of PtRe catalysts the sulfur is preferentially adsorbed on Re sites. Such sulfur on Re seems to have the unique ability to suppress formation of C_6-products from MCH while not interfering with the ability of Re to reduce coke formation.

D. A Schematic Model

Figures 12 and 13 show schematic representations of stepped, metal-crystallite surface embodying the concepts and models of Somorjai and co-workers (*15*, *16*) and Sachtler (*21*), with some modifications to accommodate the findings of this and the accompanying paper. These representations seem to be in accord with the major experimental observations.

According to Fig. 12, the metal crystallites are activated by hydrocracking at the kinked steps. The carbene and carbyne fragments formed by hydrogenolysis at the kinks combine to produce a disordered hydrocarbonaceous layer which grows outward from the edges and across the terraces. This layer deactivates the kinked cracking sites to a significant extent. The presence of Re at the kink sites increases their hydrogenolysis selectivity toward gaseous rather than layer-forming products;



sulfur and sulfur compounds bonded to Re in terrace surface; small amounts of sulfur here prevent blocking of Pt ensembles by carbon layers and interfere with rearrangement of disordered catalytic carbon to graphitic non-catalytic carbon; very large amounts of sulfur block dehydroaromatization sites and/or prevent formation of disordered, catalytic carbon layer

hydrogenolysis step sites irreversibly poisoned

FIG. 13. Schematic diagram of terraced metal crystallite surface in the presence of sulfur. Coke deposit not shown.

thereby this Re retards somewhat the rate of formation of the carbonaceous deposits. In the presence of hydrogen alone, this Re catalyzes the hydrogenolytic removal of these deposits from the neighborhood of the kinked edge sites thereby reactivating them and restoring much of the hydrogenolysis activity of the fresh catalyst. Dehydroaromatization takes place by the concerted action of ensembles of Pt atoms in the surface of the terrace and perhaps in concert with nearby disordered, hydrocarbonaceous material. This disordered hydrocarbonaceous layer provides sites for desorption of products according to Somorjai (*15, 16*) who also suggests that this deposit rearranges in part to form slowly the catalytically inactive graphitic islands shown in the figure. The presence of Re atoms in the surface of the terrace may retard somewhat the formation of these graphitic structures and may catalyze somewhat hydrogenolytic removal of carbonaceous material from blocked Pt ensembles in the terrace surface. The presence of Re at the terrace surface may also interfere with hydrogenolytic activity of Pt ensembles while not significantly disturbing their aromatization activity. Without the presence of S, however, the influence of Re in the terrace surface seems to be slight.

Figure 13 shows schematically a sulfided, stepped, metal-crystallite surface. In order to keep this diagram simple no carbonaceous material is shown on the surface. Here the sulfur shown adsorbed at the kinked edges substantially deactivates these hydrocracking sites. This deactivation is far less reversible when the sulfur is strongly bonded to Re present at the kinks. The carbonaceous layer grows outwards over the terrace sites far less slowly when the edge-sites are poisoned by sulfur. Following Sachtler (*21*), Re atoms in the surfaces of the terraces are depicted as bonding sulfur and sulfur compounds tightly. The sulfur poison tightly bonded to the terrace sites interferes with the growth of the carbonaceous layer and its rearrangement into catalytically inactive graphitic material. By retarding the growth and rearrangement of the carbonaceous layer the sulfur bound to Re in the terrace surfaces prevents the carbon from blocking ensembles of Pt terrace atoms required to catalyze the dehydroaromatization. Such sulfur-capped Re atoms may also deactivate the hydrogenolytic function of Pt ensembles in the surface of the terrace while not significantly disturbing their aromatization activity.

ACKNOWLEDGMENTS

We thank Mobil Foundation for partial support of this work through a grant. We also thank Ed Measom for help in the careful performance of microbalance experiments and W. M. H. Sachtler for helpful suggestions.

REFERENCES

1. Ciapetta, F. G., and Wallace, D. N., *Catal. Rev.* **5**(1), 88 (1971).
2. Ciapetta, F. G., *Petro/Chem. Eng.* **33**(5), c-19 (1961).
3. Kluksdahl, H. E., U.S. Patent 3,415,737 (1968).
4. Anonymous, *Oil Gas J.* p. 73. April 19, 1979.
5. Antos *et al.*, U.S. Patent 4,178,268 (1979).
6. Biloen, P., Helle, J. N., Verbeck, H., Dautzenberg, F. M., and Sachter, W. M. H., *J. Catal.* **63**, 112 (1980).
7. Coughlin, R. W., Hasan, A. M., and Kawakami, K., *J. Catal.* **88**, 150 (1984).
8. Hasan, A. M., Master's thesis, The University of Connecticut, 1982.
9. Blakely, D. W., and Somorjai, G. A., *J. Catal.* **42**, 181 (1976).
10. Pfefferle, W. C., *Amer. Chem. Soc. Div. Pet. Chem. Prepr.* **15**(1A), A21 (1970).
11. Hayes, J. C., Mitsche, R. J., Pollitzer, E. L., and Homier, E. H., *Amer. Chem. Soc. Div. Pet. Chem. Prepr.* **19**, 334 (1974).
12. Sivasanker, S., and Ramaswany, A. V., *J. Catal.* **37**, 553 (1975).
13. Weisz, P. B., "Advances in Catalysis," Vol. 13, p. 137. Academic Press, New York, 1973.
14. Dautzenberg, F. M., Helle, J. N., Biloen, P., and Sachtler, W. M. H., *J. Catal.* **63**, 119 (1980).
15. Somorjai, G. A., and Zaera, F., *J. Phys. Chem.* **86**, 3070 (1982).
16. Davis, S. M., Zaera, F., and Somorjai, G. A., *J. Catal.* **77**, 439 (1982).
17. Haensel, V., U.S. Patent 3,006,841 (1961).
18. Menon, P. G., Marin, G. B., and Froment, G. E., *I&EC Prod. Res. Dev.* **21**, 52 (1982).
19. Menon, P. G., and Prasad, J., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond and P. B. Wells, and F. C. Tompkins, Eds.), p. 1061. The Chemical Society, London, 1976.
20. Kelley, M. J., Freed, R. L., and Schwartzfager, D. G., *J. Catal.* **78**, 445 (1982).
21. Sachtler, W. M. H., paper presented at European Conference on Metal Catalysis, Brussels, September 1983; *J. Mol. Catal.*, in press.
22. Sinfelt, J. H., Carter, J. H., and Yates, D. J. C., *J. Catal.* **24**, 283 (1972).
23. Sinfelt, J. H., *J. Catal.* **29**, 308 (1973).
24. Ponec, V., and Sachtler, W. M. H., *J. Catal.* **24**, 250 (1972).