

Reactions of Methylcyclohexane and *n*-Heptane over Supported Pt and Pt-Re Catalysts

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Reactions of methylcyclohexane (MCH) and *n*-heptane were compared, using industrial Pt/Al₂O₃ or Pt-Re/Al₂O₃ catalysts. Although the same products were generally observed, product selectivity and rate of catalyst deactivation differed substantially for the two reactants. With *n*-heptane, greater amounts of light cracked products (C₁-C₅), heavy alkylated aromatics, and coke were produced. With *n*-heptane the total aromatic yield (benzene + toluene yields) was substantially less and the decline in the total aromatic yield during the first feed cycle was in general much greater. Selectivity for aromatic products immediately following hydrogen treatment of the coked Pt-Re catalysts was less with MCH than with *n*-heptane. Presulfiding the Pt catalyst slightly poisoned the dehydrogenation and dehydrocyclization activities. However, the presulfided Pt-Re/Al₂O₃ catalyst was very selective for these reactions and a high total aromatic yield was observed with either MCH or *n*-heptane. Sulfur quenched hydrogenolysis, demethylation, and reactions which form alkylated aromatics of higher molecular weight than toluene. © 1987 Academic Press, Inc.

INTRODUCTION

Severe coking or sulfiding deactivates platinum catalysts for catalytic reforming of low-octane feed stocks such as naphthenes and straight-chain paraffins. Neither coke nor sulfur should be thought of as being totally disadvantageous, however. Working with Pt single crystals, Davis, *et al.* (1, 4) found that only 2 to 25% of the Pt crystal remained uncovered by the carbonaceous overlayer. Although it is believed that most of the hydrocarbon reactions occur on the small, clean Pt ensembles, the carbonaceous overlayer may play an important role in hydrogen transfer, as a desorption site for chemisorbed hydrocarbons and as a pool of product intermediates. Biloen and co-workers (2) noted that sulfur from H₂S selectively bonded with Re and did not poison active Pt sites. They observed that the combined action of rhenium and sulfur caused the sulfided Pt-Re/SiO₂ catalyst to be very selective for mild dehydrogenation reactions. Coughlin *et al.* (6, 7) have inves-

tigated the influence of carbonaceous deposits and sulfiding during the reforming of methylcyclohexane (MCH) with commercial Pt and Pt-Re catalysts. Here we report on the continuation of the latter studies with *n*-heptane substituted for MCH. Products formed during hydrogen treatment of the coked catalyst were also investigated.

EXPERIMENTAL

Reactions. Methylcyclohexane and *n*-heptane were used as model reactants to represent industrial reforming reactions. Industrial catalysts of Pt on γ -alumina and Pt-Re on γ -alumina were employed. All reactions were conducted at 1 atm and 500°C. The gas entering the reactor consisted of a mixture of H₂/N₂/(model reactant) in a molar ratio of 9/9/1. The WHSV was 0.14 g model reactant/(g cat. h). The experimental procedure after catalyst pretreatment involved cyclic exposure to hydrocarbon feed (50 ml/min) followed by pure H₂ (50 ml/min). Using a gas chromatograph, conversions and product yields were measured every 50 min. More detailed descriptions of the catalysts used, of the ex-

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perimental procedure, and of the apparatus have been reported previously (3, 6, 7).

Pretreatment of catalysts. Catalysts were exposed to dry air (50 ml/min) for 1 h and then to pure H₂ (50 ml/min) for 3 h. For some experiments the catalysts were then presulfided using 10 ppm H₂S in H₂ (118 ml/min) for 50 h. The temperature was kept constant at 500°C.

Thermal noncatalytic reaction. The extent of the thermal reaction (reactor packed with glass beads) at 500°C was limited to 23.1% conversion of MCH with the yields C₁–C₅, 4.2%; toluene, 12.9%; methylcyclohexadienes, 0.1%; benzene, 2.2%; coke, 3.7%. Similarly, the thermal conversion of heptane was 7.2% and the corresponding yields were C₁–C₅, 3.5%; toluene, 0.80%; benzene, 0.12%; xylene, 0.38; coke, 2.4%.

RESULTS

Total conversion of reactant. Figure 1 shows the conversion of MCH over three sequential cycles of exposure to the hydrocarbon feed of durations 20, 7, and 6 h, respectively. Each cycle was followed by a

hydrogen treatment for 10, 5, and 6 h, respectively. During experiments involving sulfur, 10 ppm H₂S was present in the hydrogen treatment gas and the catalysts were also pretreated for 50 h in flowing hydrogen containing 10 ppm H₂S. Monometallic Pt or Re and bimetallic Pt–Re catalysts of different compositions were studied. All catalysts were supported on γ -alumina.

With the exception of the Re catalyst (not shown in Fig. 1), the conversion of MCH was almost complete for the first 10 h. The bimetallic Pt–Re catalyst showed the highest conversion during all three cycles. In the case of the presulfided 0.32% Pt–0.325% Re catalyst, complete conversion was observed for all three cycles. The monometallic Pt catalyst showed the same high initial conversion but was deactivated at a faster rate than the bimetallic Pt–Re catalyst. The results available indicate that increasing the Pt loading from 0.32 to 0.60% increased the rate of deactivation, especially after hydrogen treatment. Presulfiding the 0.35% Pt catalyst did not ad-

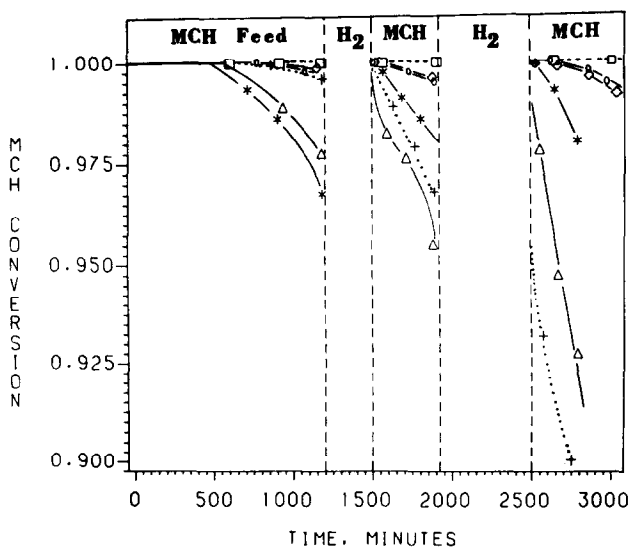


FIG. 1. Conversion of MCH vs time for various industrial reforming catalysts: 0.35% Pt (—*—), 0.60% Pt (—△—), 0.32% Pt–0.325% Re (---○---), 0.60% Pt–0.85% Re (---◇---), presulfided 0.35% Pt (···+···), presulfided 0.60% Pt–0.85% Re (---□---). Conditions: 1 atm, 500°C, WHSV = 0.14 g MCH/g cat. h. Molar ratio of feed: MCH/H₂/N₂ = 1/9/9.

versely affect conversion during the first hydrocarbon feed cycle; however, shortly after the beginning of the second feed cycle the conversion of the presulfided 0.35% Pt catalyst dropped rapidly apparently due to irreversible sulfur poisoning.

The performance of the same monometallic and bimetallic catalysts was also studied using *n*-heptane as a model reactant following the same experimental procedure. Figure 2 shows the conversion of *n*-heptane for three cycles of hydrocarbon treatment. Although both the monometallic Pt and bimetallic Pt-Re catalysts showed a higher degree of deactivation with *n*-heptane than with MCH, both model reactants showed the same basic catalytic deactivation patterns. For example, the monometallic Pt catalyst showed a greater degree of deactivation than the bimetallic Pt-Re catalyst. The presulfided bimetallic Pt-Re catalyst experiments produced complete conversion of *n*-heptane and MCH for all three feed cycles. However, the effects of presulfiding the Pt catalyst during the *n*-heptane experiments were slightly different

from what was observed during the MCH experiments. During the *n*-heptane experiments, the 0.60% Pt catalyst showed a substantial degree of deactivation shortly after the initiation of the reaction. Its conversion then leveled off for the remainder of the experiment at approximately 50%. The drop in conversion of MCH for the presulfided 0.35% Pt catalyst occurred more gradually over all three feed cycles.

Product yields. Figure 3 shows the major products observed during the *n*-heptane reactions with 0.60% Pt catalyst. Some of the products identified by GCMS were hexane, 1- and 3-methylcyclohexene, benzene, toluene, ethylbenzene, xylenes, and other alkylated aromatics. The same products were observed during the MCH and heptane experiments, although the product distribution and selectivities were different. Among the products of MCH reactions was *n*-heptane.

Benzene yield. The yield of benzene from MCH is shown in Fig. 4 and from *n*-heptane in Fig. 5. For both the MCH and *n*-heptane reactions, a high initial selectivity toward

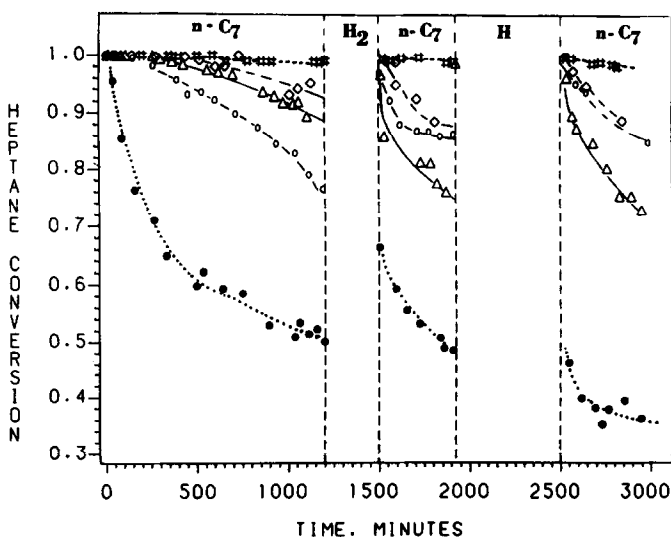


FIG. 2. Conversion of *n*-heptane vs time for various industrial catalysts = 0.60% Pt (—Δ—), 0.32% Pt-0.325% Re (---○---), 0.60% Pt-0.85% Re (---◇---), presulfided 0.60% Pt (···⊕···), presulfided 0.32% Pt-0.325% Re (---#---). Conditions: 500°C, 1 atm, WHSV = 0.14 g *n*-heptane/g cat. h. Molar ratio of feed: *n*-heptane/H₂/N₂ = 1/9/9.

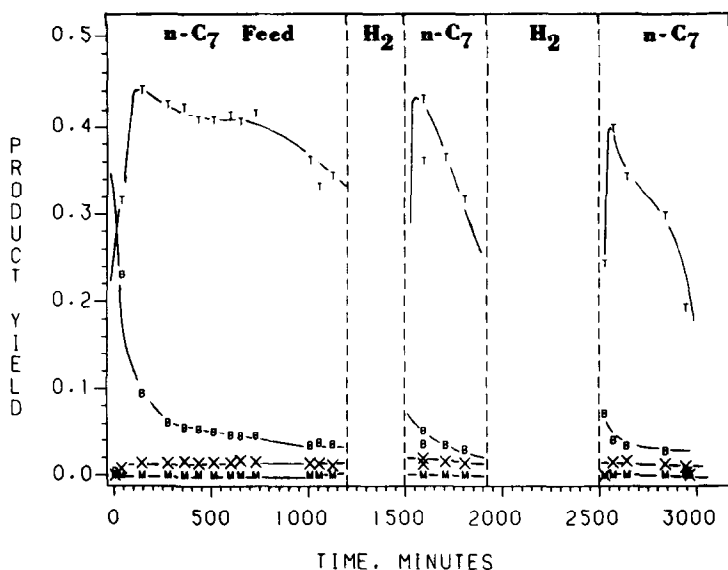


FIG. 3. The different products produced with *n*-heptane on a typical platinum catalyst (0.60% Pt)—toluene (T), benzene (B), *m*-xylene (X), 1-methylcyclohexene (M).

benzene was observed on the nonpresulfided Pt and Pt-Re catalysts. The initial amount of benzene produced in the first cycle is higher for the catalyst with higher content of Pt. With either MCH or *n*-heptane, the nonpresulfided 0.60% Pt and

0.60% Pt–0.85% Re catalysts showed the highest initial benzene yields.

Within the first several hours the benzene yield dropped considerably until finally it leveled off. At this stage, the nonpresulfided bimetallic Pt–Re catalysts caused a

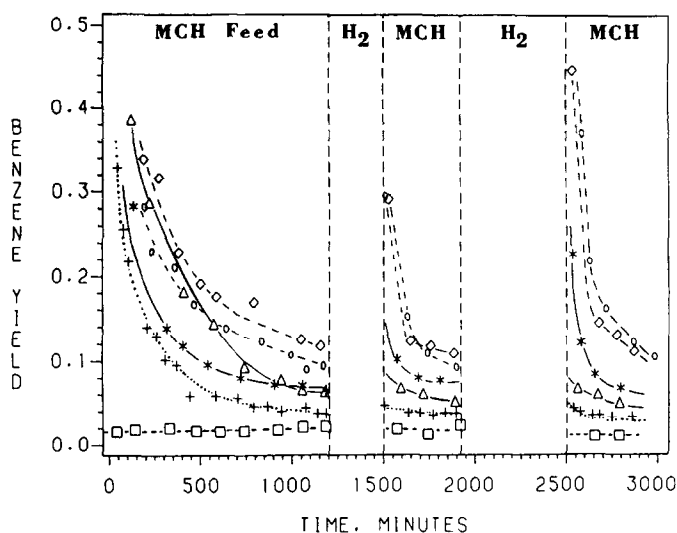


FIG. 4. Benzene yield vs time during the reforming of MCH obtained with 0.35% Pt (—*—), 0.60% Pt (—△—), 0.32% Pt–0.325% Re (···○···), 0.60% Pt–0.85% Re (---◇---), presulfided 0.35% Pt (···+···), presulfided 0.60% Pt–0.85% Re (---□---).

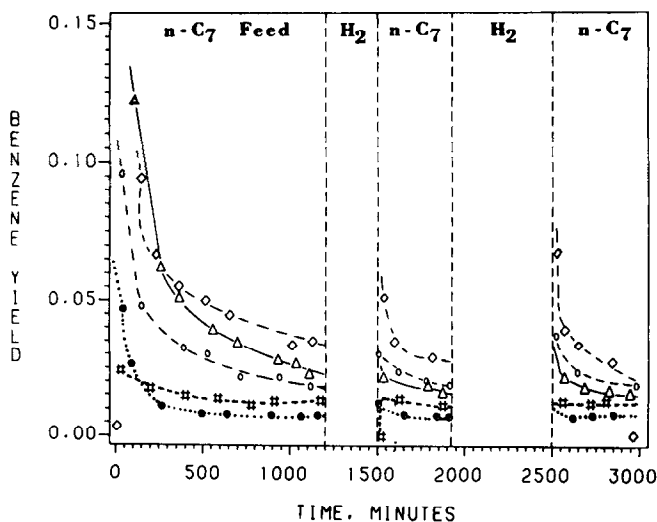


FIG. 5. Benzene yield vs time during the reforming of *n*-heptane obtained with 0.60% Pt (\triangle), 0.32% Pt-0.325% Re (\circ), 0.60% Pt-0.85% Re (\diamond), presulfided 0.60% Pt (\oplus), presulfided 0.32% Pt-0.325% Re ($\#$).

higher benzene yield than any of the monometallic catalysts, regardless of the Pt loading.

An initial maximum in the production of benzene was also observed during the second and third exposures to hydrogen feed. Treating the used catalyst with hydrogen partially restored the benzene yield especially for the nonpresulfided bimetallic Pt-Re catalyst. Thus, except for the initial hours of both the MCH and *n*-heptane experiments, the nonpresulfided bimetallic Pt-Re catalyst had a higher benzene yield than the nonpresulfided monometallic Pt catalyst. Over all three cycles, the production of benzene was much lower from *n*-heptane than from MCH.

Pretreating Pt or Pt-Re catalysts with sulfur sharply decreased the production of benzene and alkylated aromatics. Carbon balance calculations indicate that sulfiding also reduces the amount of lighter products (C_1 - C_5).

Total aromatic yield. Total aromatic yield (i.e., sum of the benzene and toluene yields) is shown in Fig. 6 for MCH feed and Fig. 7 for *n*-heptane feed; the yields of other heavier aromatics (xylenes, ethylbenzene,

cumene, etc.) which have a lower-octane rating were insignificant (<3%).

As seen in Fig. 6 (MCH experiments), the total aromatic yield for the nonpresulfided monometallic Pt catalysts reached its maximum value several hours after the initiation of the experiment and then dropped slowly but steadily. The nonpresulfided 0.60% Pt catalyst showed as much as 15% deactivation of its dehydrogenation activity. This same pattern was observed for the nonpresulfided bimetallic Pt-Re catalysts. However, the maximum total aromatic yield for the Pt-Re catalysts occurred later and the Pt-Re catalysts showed less dehydrogenation deactivation than the monometallic catalysts. Thus, by the end of the first cycle, the bimetallic 0.32% Pt-0.35% Re catalyst exhibited a higher total aromatic yield than all the other nonpresulfided catalysts. Presulfiding further enhanced the total aromatic yield of the bimetallic Pt-Re catalyst. The presulfided 0.60% Pt-0.85% Re catalyst showed an initially high selectivity toward aromatics. This nearly complete conversion of MCH to toluene was maintained throughout the first feed cycle. The yield of total

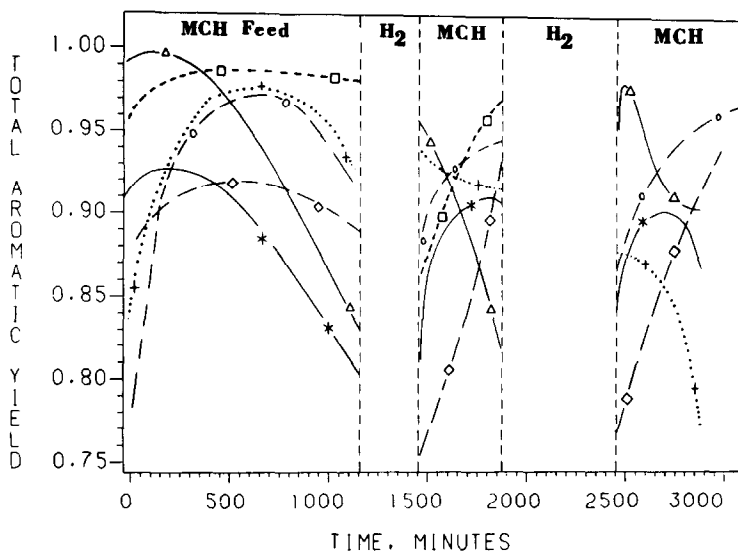


FIG. 6. Total aromatic yield vs time during the reforming of MCH obtained with 0.35% Pt (—*—), 0.60% Pt (—△—), 0.32% Pt-0.325% Re (---○---), 0.60% Pt-0.85% Re (---◇---), presulfided 0.35% Pt (···+···), presulfided 0.60% Pt-0.85% Re (---□---).

aromatics produced using a monometallic Re catalyst (not shown in the diagram) was only 10%.

At the beginning of the second and third

MCH feed cycles, the nonpresulfided 0.60% Pt catalyst caused the highest total aromatic yield. However, the 0.60% catalyst deactivated rapidly and by the end of

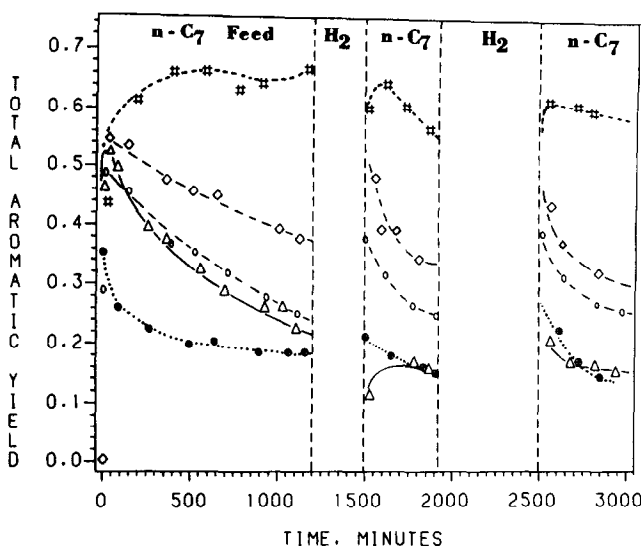


FIG. 7. Total aromatic yield vs time during the reforming of *n*-heptane obtained with 0.60% Pt (—△—), 0.32% Pt-0.325% Re (---○---), 0.60% Pt-0.85% Re (---◇---), presulfided 0.60% Pt (···⊕···), presulfided 0.32% Pt-0.325% Re (---#---).

each cycle its total aromatic yield was less than that of any of the other nonsulfided catalysts.

In contrast, the nonpresulfided bimetallic catalysts caused a low aromatic yield initially, which rose as the reaction proceeded. By the end of both the second and the third MCH feed cycles, the 0.32% Pt–0.325% Re catalyst showed the highest dehydrogenation activity among the nonpresulfided catalysts examined. The presence of sulfur increased the bimetallic Pt–Re catalyst's selectivity for total aromatics throughout each MCH feed cycle. The presulfided 0.35% Pt catalyst produced a high initial total aromatic yield following hydrogen treatment, but after several hours its total aromatic yield dropped rapidly.

Figure 7 shows that regardless of the catalyst type the total aromatic yields produced when the model reactant is *n*-heptane are significantly lower than those when the model reactant is MCH. The maximum total aromatic yield from *n*-heptane with either monometallic Pt or bimetallic Pt–Re catalysts occurs very shortly after the initiation of the reaction. The nonpresulfided catalysts with higher platinum loading have a slightly higher initial dehydrocyclization activity. However, as the experiment continued, the activity of the 0.60% Pt catalyst decreased at a faster rate than did that of the bimetallic Pt–Re catalysts and, by the end of the initial feed period, the 0.60% Pt catalyst produced the lowest aromatic yield among all the nonpresulfided catalysts. Of the nonpresulfided catalysts, the 0.60% Pt–0.85% Re catalyst showed the lowest degree of deactivation and the highest stability.

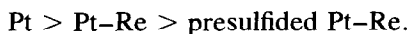
Treating the bimetallic catalysts with hydrogen increased the total aromatic yield but had no significant effect on the monometallic Pt catalyst.

The presulfided bimetallic 0.32% Pt–0.32% Re catalyst showed a stable and relatively high aromatic yield (about 70% for presulfided Pt–Re compared to about 25

to 50% for the nonsulfided catalysts). This was observed for all three cycles. On the other hand, the presulfided 0.60% Pt catalyst showed the lowest aromatic yield of all tested catalysts. Apparently, Pt in the monometallic catalyst is strongly poisoned by sulfur and deactivates dehydrocyclization-type reactions.

Coke formation and coke hydrogenation products. After each exposure to MCH, the catalyst was treated with hydrogen which partly restored its activity. While hydrogen was flowing through the reactor, some hydrocarbons (benzene, toluene, and aromatics heavier than toluene) were identified in the effluent gas. These amounts can be presented as yields by dividing the amount of toluene or benzene observed in the effluent gas by the amount of hydrocarbon feed the catalyst had been previously exposed to during the feed cycle. This procedure allows direct comparison of the amounts measured during the different cycles. Figure 8 shows that the yields of benzene and toluene removed from the 0.60% Pt catalyst after it had been exposed to *n*-heptane for 20 h were relatively low and decreased with time. The inner diagram of Fig. 8 shows the many different components (MCH, benzene, toluene, xylenes, and other heavier aromatics) observed during hydrogen treatment of the Pt catalyst previously exposed to *n*-heptane. Comparing these results to the results observed after the catalyst was exposed to MCH suggests that the surface of the catalyst previously exposed to *n*-heptane was more populated with heavier aromatics than the surface of the same catalyst exposed to MCH.

Figure 9 records the yields of toluene observed during the hydrogen treatment of the catalysts exposed to MCH for 20 h. The amount of toluene hydrogenolytically removed from the surface of the preexposed catalyst decreases in the order:



Similar results were observed during the

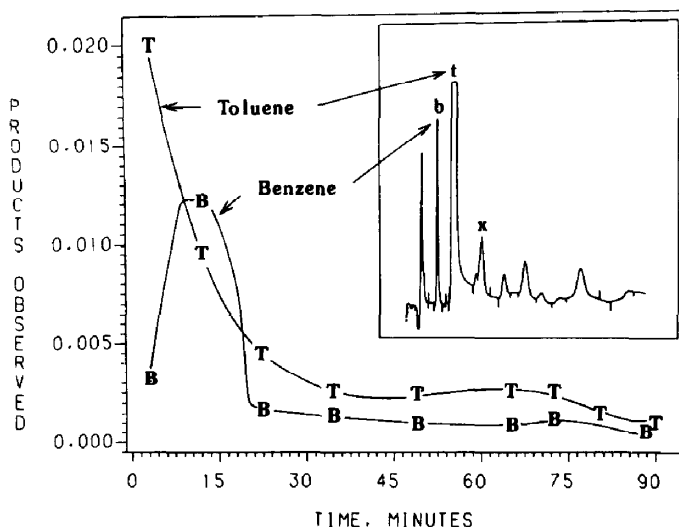


FIG. 8. Amounts (arbitrary relative units) of benzene (B) and toluene (T) hydrogenolytically removed from the surface of a 0.60% Pt catalyst during hydrogen treatment. The catalyst was previously exposed MCH for 20 h. Insert illustrates the various components removed from the surface of the catalyst.

second and third hydrogen treatment periods.

DISCUSSION AND CONCLUSIONS

Total conversion of reactant. With both MCH and *n*-heptane high conversion was observed at the beginning of each feed

cycle for all catalysts except Re. The conversion decreased with time, presumably due to the formation of coke, which deactivated the catalyst. Coke forms more rapidly on the Pt monometallic catalyst (6, 7), and the conversion of the Pt catalyst began to drop after several hours of exposure to

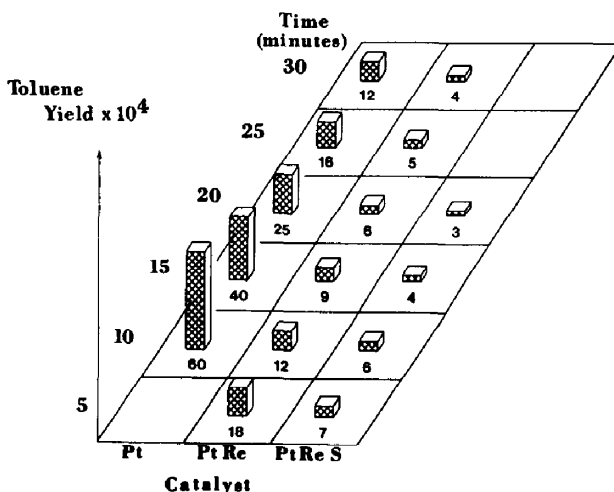


FIG. 9. Amount of toluene observed during hydrogen treatment vs time for a 0.35% Pt, a 0.36% Pt-0.36% Re, and a presulfided 0.6% Pt-0.85% Re catalyst. All catalysts were exposed to MCH for 20 h. The height of the bars represents the amounts (arbitrary relative units) of toluene observed multiplied by a factor of 10,000.

hydrocarbon feed. In contrast, the conversion produced by bimetallic Pt–Re catalyst remained high over many hours with either MCH or *n*-heptane feeds. As already reported in previous work (7), presulfiding the Pt–Re catalyst increases total conversion, while it decreases the amount of coke formed. On the other hand, sulfur poisons the monometallic Pt catalyst especially during the reaction of *n*-heptane.

Cracked products. Performing carbon mass balance calculations indicates that *n*-heptane produced significantly larger quantities of C₁–C₅ products than did MCH. This is an expected result because the pathway from *n*-heptane to C₁–C₅ products requires fewer steps than from MCH to C₁–C₅, regardless of whether straight-chain olefins (8) or C₅-rings (9, 10) are involved as intermediates. The carbon balance also indicates that presulfiding significantly decreased the yields of lighter C₁–C₅ products.

Benzene yield. With either MCH or *n*-heptane as feed, benzene was a major product produced at high yield early in each feed period (Figs. 4 and 5). The benzene yield was significantly suppressed by the formation of coke or by presulfiding. The fact that sulfur nearly quenches benzene production suggests that demethylation occurs exclusively on metal crystallites easily poisoned by sulfur. Other reactions like dehydrogenation and dehydrocyclization, which are believed to occur on metallic crystallites (1, 4, 11), were not adversely affected by presulfiding. These results suggest that hydrogenolysis and demethylation require larger metallic ensembles free of sulfur and coke than dehydrogenation and dehydrocyclization.

Figures 4 and 5 show that in the absence of sulfur the Pt–Re catalyst is more active for demethylation than the Pt catalyst. This is the opposite of what would be expected if Re were inactive (as it appeared to be in the monometallic 0.85% Re catalyst) and simply decreased the size of the active Pt ensembles by dilution.

Apparently, Re in the bimetallic catalyst participates in demethylation. According to Shum *et al.* (12) the Re–C bonds are stronger than the Pt–C bonds and thus more than one carbon atom per reactant molecule is adsorbed to an active ensemble if the concentration of Re is high. Since multiadsorption is usually required before C–C bond breakage occurs, the hydrogenolysis activity is expected to increase as the percentage of Re in the catalyst is increased. However, when bonding between an adsorbed molecule and a Re-containing catalyst becomes very extensive, then desorption of the carbon fragments becomes impeded and eventually the rate-limiting step in hydrogenolysis. The Re/Al₂O₃ catalyst was found to have a low hydrogenolysis and demethylation activity in accord with this hypothesis.

During reaction of either MCH or *n*-heptane, coking, presulfiding, and the presence of Re in the catalyst affected the benzene yield in a very similar fashion. This suggests that the mechanism for demethylation is similar for either reactant.

Total aromatic yield. Total aromatic yield (i.e., the sum of benzene and toluene yields) as plotted in Figs. 6 and 7 indicates the extent of MCH dehydrogenation or *n*-heptane dehydrocyclization, respectively. The rate of deactivation for the dehydrocyclization reactions (*n*-heptane feed) is greater than that for the dehydrogenation reactions (MCH feed). On the metallic crystallites of the working catalyst, only very small active ensembles remain uncovered by the carbonaceous overlayer (1, 13, 14), and ensemble size requirements may explain why there is a difference in the rate of deactivation of the dehydrogenation and dehydrocyclization rates. It is believed that ensemble size requirements for the following reactions decrease in the following order (15):

Hydrogenolysis = demethylation
> dehydrocyclization > dehydrogenation.

Several models of the working Pt/Al₂O₃ and

Pt-Re/Al₂O₃ catalysts have been proposed (1, 5, 7).

Blakely and Somorjai (16), studying reforming of cyclohexane, suggested that cyclohexane dehydrogenation to benzene occurs via a cyclohexene intermediate and that the later stages of dehydrogenation may deactivate by severe coking. If MCH dehydrogenation follows a similar pattern, then the yields of intermediates such as 1-MCHene and 3-MCHene should increase as the later steps of the dehydrogenation reaction become rate limiting. This is exactly what was observed on the 0.60% Pt catalyst. The yields of 1-MCHene and 3-MCHene increased toward the end of each feed cycle as the carbonaceous overlayer became disordered and slowed the later steps of the MCH dehydrogenation reaction. According to Sharan (8), the last step of both the dehydrogenation and the dehydrocyclization mechanisms is the same. 1-MCHene and 3-MCHene were observed during the reactions of MCH or *n*-heptane but only with nonpresulfided monometallic Pt catalysts. The highest degree of deactivation for either MCH dehydrogenation or *n*-heptane dehydrocyclization occurred on the 0.60% Pt catalyst.

In order to estimate the extent of catalyst deactivation, an experiment was performed in which the two reactants (MCH, *n*-heptane) were interchanged. At the end of an *n*-heptane experiment the feed was changed over to MCH. The product distribution which was observed during this MCH feed cycle suggests that *n*-heptane causes the catalyst to deactivate at a faster rate than does MCH.

These observations parallel the observations of Cooper and Trimm (17) who reported that the tendency of *n*-hexane to form coke is greater than that of cyclohexane. Thus, it seems reasonable that the greater amounts of coke formed during the *n*-heptane experiments contributed to the observed fast deactivation of the dehydrocyclization reaction.

Coke formation and coke hydrogenation

products. In previous studies (6, 7) the amount of coke deposited on the catalyst during 20 h of exposure to MCH and the amount of coke removed during the first hydrogen treatment were determined using thermal gravimetric analysis (TGA). These results are summarized in rows 2 and 3 of Table 1 for comparison to the results reported in this paper and discussed below. Although more coke was deposited on the surface of the Pt catalyst, more coke was removed from the bimetallic Pt-Re catalyst during hydrogen treatment. Re may accelerate the catalytic removal of coke from the surface of the catalyst or the presence of Re may hamper the reconstruction of the carbonaceous overlayer to form graphitic coke (5); nongraphitic coke would be easier to remove.

Gas chromatography (GC) and gas chromatography/mass spectrometry (GCMS) were used in the present work to determine the compounds hydrogenolytically re-

TABLE 1
Coke Observed during First Hydrogen Treatment

Row	Type of catalyst	Unsulphided 0.60% Pt	Unsulphided 0.32% Pt- 0.32% Re
1.	Surface area (m ² /g)	219	238
2.	Coke deposited on 5 g of catalyst after 20 hr of MCH (g/5 g cat.) (from Ref. (7))	0.3015	0.285
3.	Coke removed during the first hydrogen treatment (5 h) (g/5 g cat.) (from Ref. (7))	8.63×10^{-3}	0.014
4.	Total amount of toluene measured during the first hydrogen treatment (g toluene/5 g cat.)	8.76×10^{-4}	4.38×10^{-4}
5.	Total amount of benzene measured during the first hydrogen treatment (g benzene/5 g cat.)	3.60×10^{-4}	2.64×10^{-4}
6.	Sum of benzene and toluene observed during the first hydrogen treatment (g/5 g cat.)	1.24×10^{-3}	7.02×10^{-4}

Note. The results above (except the surface area of the catalyst) refer to a basis of 5 g of catalyst. The amount of coke deposited on the presulfided Pt-Re catalyst was 0.0175 g and the amount removed during the first H₂ treatment was 0.0044 g.

moved from the surface of the coked catalyst during hydrogen treatment. The total amount of toluene and benzene and the sum of toluene plus benzene ($T + B$) generated during the first hydrogen treatment are shown in rows 4, 5, 6 and Table 1. These values were estimated by graphical integration of fractional yields plotted vs time as shown in Fig. 8. Toluene and benzene were the only measurable products observed with MCH. When *n*-heptane was used, heavier aromatics (xylenes, ethylbenzene, cumene, etc.) were also measured. Aromatics heavier than toluene were identified by mass spectrometry for both MCH and *n*-heptane feeds.

The compounds observed during the hydrogen treatment appear to arise from hydrogenolysis of the carbonaceous deposits rather than simple displacement or desorption because these compounds were evolved over a long period of time (5 or even 8 h).

The results shown in Table 1 can also be used to estimate the fraction of a monolayer corresponding to the amount of benzene and toluene produced during hydrogen treatment and the amount of carbon removed relative to the Pt particle size and dispersion in the catalyst. The calculations are as follows.

For 5 g of catalyst containing 0.60% Pt the amount of Pt may be written

$$\frac{0.60}{100} \times 5 = 0.030 \text{ g Pt}$$

$$\text{or } 1.54 \times 10^{-4} \text{ g atoms Pt}$$

$$\text{or } 9.26 \times 10^{19} \text{ Pt atoms.}$$

The coke removed (measured gravimetrically) during the first hydrogen treatment was

$$8.63 \times 10^{-3} \frac{\text{g coke}}{5 \text{ g cat.}}$$

which corresponds to

$$8.63 \times 10^{-3} \frac{\text{g coke}}{5 \text{ g cat.}}$$

$$\begin{aligned} & \times \frac{5 \text{ g cat.}}{9.26 \times 10^{19} \text{ Pt atoms}} \\ & \times \frac{6.03 \times 10^{23} \text{ C atoms}}{12 \text{ g coke}} \\ & = 4.7 \frac{\text{C atoms}}{\text{Pt atom}} \end{aligned}$$

or

$$\begin{aligned} 4.7 \frac{\text{C atoms}}{\text{Pt atoms}} & \times \frac{1 \text{ toluene molecule}}{7 \text{ C atoms}} \\ & = 0.67 \frac{\text{toluene molecules}}{\text{Pt atom}}. \end{aligned}$$

A similar calculation can be performed using the amount of benzene and toluene ($B + T$) observed during the hydrogenolytic coke removal:

$$1.235 \times 10^{-3} \frac{\text{g}(B + T)}{5 \text{ g cat.}}$$

which corresponds to

$$0.0944 \frac{(B + T) \text{ molecules}}{\text{Pt atom}}. \quad [1]$$

Assuming that Pt exists on the surface of the catalyst as cubic crystals of average size of 40 Å, each crystal then contains approximately 1400 Pt atoms and has a surface area of 8000 Å².

Assuming that an adsorbed precursor of a benzene molecule occupies 18.1 Å², and that five faces of each cubic Pt crystallite are covered by a monolayer of such adsorbed precursors, then each such Pt crystallite is covered by

$$8000/18.1 = 442 \text{ benzene molecules per monolayer.} \quad [2]$$

The density of Pt (7 g/cm³) can be used to estimate the volume occupied by a single Pt atom:

$$46.5 \frac{\text{Å}^3}{\text{Pt atom}}. \quad [3]$$

Thus, the number of Pt atoms in a 40-Å cubic crystallite is

$$\frac{(40 \text{ \AA})^3}{46.5} = 1376 \text{ Pt atoms per crystallite.}$$

Thus we have

$$442/1376 = 0.32 \frac{\text{(benzene molecules per monolayer)}}{\text{(Pt atom)}} \quad [4]$$

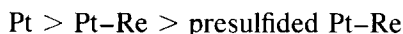
Experimentally observed benzene formed by hydrogenolysis of coke relative to the estimated amount of benzene that exists in a single precursor monolayer of the Pt crystallite is

$$\frac{0.0944 \text{ (benzene molecules) / (Pt atom)}}{0.32 \text{ (benzene molecules per monolayer) / (Pt atom)}} = 0.295$$

or about 30% of a monolayer is removed in the form of benzene and toluene.

In contrast, the amount of coke removed from the catalyst (measured gravimetrically) was equivalent to about 0.67 (benzene molecules)/(Pt atom) or about two monolayers of the Pt crystallite. The amount of carbon removed as benzene and toluene corresponds to approximately 30% of a monolayer and represents only a small fraction of the carbon removed from the catalyst (measured gravimetrically). Note that other compounds (lighter gases, or heavier aromatics such as xylene or cumene) are also removed from the catalyst during the hydrogen treatment. The contribution of these compounds is significant, and may account for the difference between the amount of coke removed as measured by TGA experiments, and the sum of benzene and toluene measured by gas chromatography of the gases formed.

It should be emphasized that although the amount of coke deposited on the catalyst decreases in the order



the amount of coke removed from the cata-

lyst during the hydrogen treatment decreases in the reverse sequence



In any case, it appears that when rhenium is present in the reforming catalyst, hydrogen treatment restores the activity of the catalyst to a greater extent. During the MCH experiments, this meant that immediately following the hydrogen treatment period there was an initial increase in the hydrogenolysis activity of the Pt-Re catalyst and thus a decrease in the total aromatic yield (Fig. 6). The Pt catalyst, however, did not lose as much coke during hydrogen treatment and there was no significant increase in the subsequent catalytic hydrogenolysis activity with the result that the total aromatic yield remained high for this catalyst immediately following hydrogen treatment.

For *n*-heptane reforming coke removal had a slightly different effect on the selectivity of the Pt-Re catalyst: here the primary reaction deactivated by coke was dehydrocyclization. Thus, immediately following each hydrogen treatment there was a large increase in the total aromatic production over the Pt-Re catalyst. In contrast, the total aromatic production over the Pt catalyst after hydrogen treatment remained relatively unchanged from that of the previous feed period (Fig. 7).

Our results agree with the conclusions of Biloen and co-workers (2) who proposed that the combined effect of Re and sulfur is responsible for an ensemble effect. This ensemble effect greatly enhances the selectivity of the presulfided Pt-Re catalyst. On one hand, the sulfur, presumed selectively bonded (2) to the rhenium, quenched hydrogenolysis and demethylation reactions. On the other hand, coke deposits (6, 7) less rapidly on sulfur-treated Pt-Re catalysts and the sulfur does not appear to influence the more effective removal of coke from Re-containing catalysts during hydrogen treatment.

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