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

I. In the Absence of Sulfur

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Starting with freshly reduced catalysts in a flow reactor, conversion of methylcyclohexane decreased less rapidly during a 20-h period while selectivity and yield of aromatics increased more rapidly with PtRe/Al_2O_3 than with Pt/Al_2O_3. During this initial 20-h period, coke deposition was retarded on the PtRe as compared to the Pt catalysts. When the coked catalysts were then exposed to pure flowing hydrogen at reaction temperatures, the coke was partially removed from both types of catalyst. When, after such hydrogen treatment, the catalysts were again exposed to MCH feed, the different catalysts behaved quite differently. Immediately after the hydrogen treatment the selectivity and yield for aromatic products was lower for the PtRe and higher with the Pt catalyst. After shifting from pure H_2 to the hydrocarbon feed, however, the PtRe catalyst began to gain aromatic selectivity whereas the Pt catalyst began to lose such selectivity. Several hours after changing from pure H_2 to HC the selectivity of the PtRe catalyst had again become significantly greater than that of the Pt catalyst, although the situation was the converse just after the change. Treatment with pure hydrogen also increased hydrogenolysis to C_6-products in the case of PtRe but decreased this cracking in the case of Pt. As exposure to hydrocarbon continued, however, the effect of the pure hydrogen treatment was lost as the cracking increased with Pt but decreased with the PtRe catalysts. These results are interpreted in terms of a carbonaceous overlayer which does not retard the dehydroaromatization reaction in its early stages but becomes site blocking in later stages. Early deposition may be primarily at kinks at the edges of exposed crystal planes with later deposition on terraces.The catalytic action of Re may preserve only certain sites free of deactivating deposits during exposure to HC + H_2, and may catalyze removal of such deposits from certain sites during treatment in pure H_2. In pure H_2, cracking sites seem to respond more to hydrogenative reaction when Re is present but this trend seems to reverse when MCH is also present.

INTRODUCTION

The present intense scientific and technological interest in multimetallic catalysts stems from a landmark discovery (*2*) that adding Re to a Pt naphtha-reforming catalyst tends to slow the rate of activity decline for such catalysts over processing time. Iridium (*21*) and tin (*10*) have also been reported to cause somewhat similar behavior in lengthening the on-stream lifetime of platinum-reforming catalysts. The precise role of the metal additive is poorly understood in terms of the usual phenomena to which catalyst deactivation is ordinarily ascribed: growth of supported metal particles and poisoning of the active catalytic surface by tight adsorption of impurities such as sulfur or by-products such as the carbonaceous products deposited on catalysts during hydrocarbon reactions and usually referred to as "coke." Such "coke" can play important roles other than that of poison, however, as pointed out by Davis, Zaera, and Somorjai (*18, 22*) based on HREELS investigation of Pt single crystals exposed to hydrocarbons. They found that the catalytically active surfaces are covered with about a monolayer of carbo-

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naceous deposit which acts not as a poison but as an essential component of the catalytically active surface. Below about 100°C, the detected carbene and carbyne species in the carbonaceous layer and it was found that, upon heating through 100°C, hydrogen was released from the layer and fragments such as CH_2, CH, and C_2H became evident. At 400°C substantially all the hydrogen leaves the layer which then appears to assume graphitic properties and act as a poison. The present paper reports work at higher temperatures and pressure (1 atm) using not single crystals but highly dispersed, supported, commercial Pt- and PtRe-reforming catalysts. Activity decline, and carbonaceous deposit formation and its hydrogenative removal on these catalysts have been observed to display behaviors that can be reconciled in large part with the observations of Somerjai and co-workers (*18, 22*) made for single crystals and at low pressure.

Previous reseach has already established that the influence of Re does not become evident (*2, 3*) until the catalyst has been exposed to hydrocarbon for several hours during which time a substantial carbonaceous deposit accumulates. Under such circumstances it has been reported (*4*) that temperature and contact time do not need to be increased as severely with Re-containing Pt-reforming catalysts as compared to monometallic Pt catalysts, in order to maintain a specified octane rating of the reformed naphtha product, as coke accumulates on the catalyst.

Other researchers (*5, 6*) have suggested that the acidic alumina support of such catalysts may be modified by the Re, and shown (*7*) that the Re is present, at least in part, as an oxide such as ReO_2 associated with the surface of the alumina. There has been much controversy about the oxidation state of Re on the catalyst. Recently Isaacs and Petersen (*16*) demonstrated the important role of water which influences the mobility of Re_2O_7 formed during calcination. Mobile Re_2O_7 can migrate to within close proximity of Pt centers which can catalyze the reduction of the Re during subsequent hydrogen treatment. Because the carbonaceous deposits on PtRe bimetallic catalysts appear to be associated with better catalytic performance than comparable deposits on Pt/Al_2O_3, Ludlum and Eischens (*8*) conducted an infrared study of differences in the chemical natures of such deposits; they observed that some carbon atoms of such deposits are bonded to oxygen (as indicated by carboxylate bands at 1570 and 1450 cm^{-1}) and that the presence of Re decreases the fraction of such carboxylate in the deposits.

In a series of publications (*25, 26*) Betizeau and Bolivar and co-workers showed that in bimetallic PtRe catalysts the Pt strongly activates reduction of Re_2O_7 to Re^0 during reductive pretreament and they argued in favor of a strong interaction between metallic Pt and Re (probably as an alloy) in these catalysts. They proposed that the effects of Pt and Re do not appear to be completely additive, however, with a portion of each apparently acting independently of the other, but with another portion of each strongly electronically modified by the presence of the other. For example, they found that until the atomic fraction of Re reaches 0.25 the major product of cyclopentane hydrogenolysis remains *n*-pentane, but as Re is increased further the proportion of secondary reactions (to form methane, ethane, *n*-propane, and *b*-butane) increases continuously.

Recent reports by Somorjai and co-workers (*17, 18*) have shown the important roles of carbonaceous deposits as a poison which blocks Pt sites as well as a promoter or cocatalyst which can store hydrogen and facilitate desorption of reaction products that are envisioned to migrate from clean portions of metal crystallites to the carbonaceous overlayers. It was also found (*17*) that adsorbed carbonaceous species can inhibit hydrogenolysis activity. These experiments (*17, 18*) used single crystals of metallic catalysts at low pressures in batch reactors; the observations and their interpretation (*17, 18*) agree reasonably well with the results reported below for highly dispersed, supported metals of industrial catalysts using flow reactors at higher pressures.

Much attention has focused on the possibility of alloy formation between Pt and Re as well as between Pt and several other second-metal promoters. For example, alloying Pt with Cu (*9*) or with Sn (*10*) produces selectivity changes dubbed "ensemble effects" and viewed as shifts from multisite mechanisms on collections of contiguous Pt atoms in Pt-rich alloys toward single-site mechanisms on Pt diluted with the promoting metal. An electronic type "ligand" effect may also be operative due to the intimate proximity of diluent atoms to Pt atoms. In the case of PtRe catalysts it has also been shown (*11*) that the combined action of Re plus S converts Pt into a catalyst selective for mild hydrogenation and argued that sulfur-covered rhenium atoms divide the surface of the platinum metal into ensembles of contiguous Pt atoms. Other evidence that Pt and Re are in intimate contact within bimetallic clusters or ensembles has also been provided by temperature-programmed reduction (*12, 16*) and a study of catalyst fouling with MCP and MCH (*19*).

The presently reported work conducted with MCH explores some aspects of the different dynamic behaviors of coke formation and product distribution caused by the presence of Re in commercial Pt-containing reforming catalysts. Starting with fresh catalysts, coke formation and product distribution were monitored over a period of about 20 h by continuous weighing of a catalyst sample in a thermogravimetric apparatus (TGA) and by periodic gas chromatographic assay of the products. After 20 h the hydrocarbon feed was switched off but the flow of hydrogen was maintained while the removal of coke and coke precursors from the catalysts by hydrogenation was monitored gravimetrically. This was repeated several times to assess the response of the catalyst activity and selectivity to successive periods in contact with a (hydrocarbon and hydrogen) feed and a feed of pure hydrogen.

TABLE 1

Catalysts Supported on γ-Alumina

Sample No.	Lot-1		Lot-2	
	J8168	M16444	K-9363	N-10695
% Pt	0.35	0.32	0.35	0.36
% Re	—	0.325	—	0.36
% Cl	0.88	0.88	0.97	1.04
% S	<0.05	<0.05	<0.05	<0.5
Surface area (m^2/g)	223	238	218	241
Pore volume (ml/g)	0.6	0.6	0.6	0.6
CO chemisorption (cm^3(STP)/g)	0.173	0.231		
Est Pt dispersion	0.43	0.38		

γ-Alumina: 0.14% Na, 0.02% Fe, <0.01% Cl, <0.01% S
Surface area = 194 m^2/g
Pore volume = 0.60 ml/g

Note. Lot-1 catalysts were used for the experiments reported in this paper. Lot-2 catalysts were used for the experiments reported in the subsequent paper (Part II).

EXPERIMENTAL

Catalysts

Reactions were conducted using two commercial Pt/Al_2O_3 catalysts, one of which also contained rhenium. Metal contents, BET surface areas, and other compositional data are given in Table 1. The support was γ-Al_2O_3, 0.16 cm diameter extrudate of average length about 0.79 cm. The chemisorption values (from which Pt dispersion is estimated) were measured by a flow method using $C^{14}O$ after reduction in H_2 for 16 h at 483°C. Alumina itself showed negligible adsorption in these experiments. Data reported in this paper were obtained using the Lot-1 catalysts. Lot-2 catalysts were used for the experiments reported in the Part II.

Reactions and Apparatus

All reactions were conducted at atmospheric pressure and 500°C. Methylcyclohexane (MCH) was added to the carrier gas (equimolar H_2 + N_2) by conducting the gas through a saturator containing MCH held at a constant temperature. For flow-reactor experiments the $[H_2]/[MCH]$ molar ratio was 9.0, the WHSV was 0.14 g MCH/g catalyst-h, and the mole fraction of MCH was 0.05; in TGA and microbalance experiments the space velocity was 3 g MCH/g cat-h and the mole fraction of MCH in the gas was about 0.05.

The MCH was Baker Analyzed Reagent grade of 99% purity; the hydrogen and nitrogen were of purity 99.99%. Air used for catalyst pretreatment was of similar purity and contained less than 0.1 ppm total hydrocarbons. The H_2 was purified of O_2 by passage through Deoxo units followed by 5A molecular sieve gas driers. The N_2 and air were similarly dried. Assay of the MCH by the Dohrman method indicated a sulfur content of less than 0.2 ppm.

The downflow reactor was a 304 stainless-steel cylinder 7 cm in diameter and 5.1 cm long; catalyst was held in seven 0.95-cm-diameter holes drilled in a symmetrical pattern parallel to the cylindrical axis. Six cartridge heaters were held in smaller holes drilled parallel to and symmetrical with the catalyst holes. The charge to the reactor was 5 g catalyst. More details can be found in Ref. (*1*).

Accelerated coke deposition and hydrogenation experiments were also conducted using a DuPont Model 951 thermogravimetric analyzer in which four preweighed catalyst pellets (90–95 mg total weight) were held in the continuously weighed platinum sample pan. The surrounding furnace was controlled to hold a preset temperature measured by a thermocouple also located in the sample pan in close proximity to the catalyst. The sensitivity of the gravimetric measurements was ±5 μg. Reaction products from the TGA were not monitored because small amounts of catalyst were used and conversions were low. Instead we relied upon parallel experiments in the reactor described above.

Procedure

The catalyst charge was slowly raised from room temperature to 500°C and held for 1 h at that temperature in a flow (50 ml/min) of dry air. Thereafter, the catalyst was treated in flowing hydrogen (50 ml/min) for 3 h at 500°C. During the first cycle of reaction followed by hydrogen treatment the gas containing MCH, H_2, and N_2 in a 1–9–9 molar ratio was fed to the reactor for 20 h followed by pure hydrogen (80 ml/min) for 5 h. For the second cycle the MCH mixture was fed for 7 h. For the TGA experiments the procedure was the same except the gas flow rate was 20 ml/min. To avoid contact between the TGA balance mechanism and hydrocarbon, the balance housing was purged by pure N_2 at a flow rate of 1 ml/min. Conversions and product yields were measured at 500°C using both Pt and Pt–Re catalysts. The reaction products were sampled and analyzed at various elapsed times.

Assay of Reaction Products

Using a heated gas-sampling valve, 20-μl aliquots were separated into major components using 3.66 m of 0.32-cm-stainless-steel tubing containing 10 wt% Carbowax 20 M on 80/100 mesh Supelcoport maintained at 80°C. The TC detector was held at 180°C. Purely thermal (reactor packed with glass beads) conversion of MCH at 500°C was only about 23% with the yields: toluene 13%; benzene 2%; MCH dienes 0.1%; cracked products 11% (only C_1 and C_2).

RESULTS AND DISCUSSION

Figure 1 shows the conversion of MCH versus time for the Pt and the PtRe catalysts. The conversion falls considerably less rapidly in the case of the Re-containing catalyst which therefore exhibits a generally lower rate of deactivation. Treatments with pure hydrogen restore the MCH conversion activity of both catalysts but for the Re-containing catalyst the restoration is much more substantial—almost to the reactivity of the fresh, unused catalyst. As shown by TGA experiments reported be-

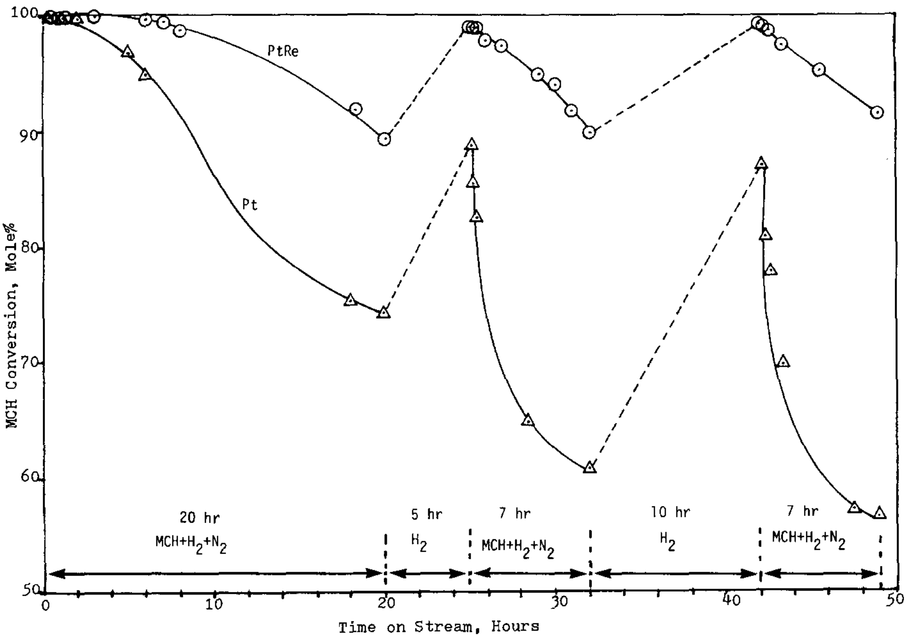

FIG. 1. Conversion of MCH vs time. Catalyst = 5 g, 500°C, 1 atm, WHSV = 0.14 g MCH/g cat-h. Feed: H_2 + N_2 + MCH in molar ratio 9/9/1. (△) 0.35% Pt + 0.88% Cl/Al_2O_3, (⊙) 0.32% Pt + 0.325% Re + 0.88% Cl/Al_2O_3, (—) catalysts on hydrocarbon feed, (- - -) pure H_2 feed.

low, coke accumulates on the catalysts during the period of contact with hydrocarbon and is partially removed during the period of contact with pure hydrogen. The presence of Re appears to be associated with slower coke deposition and this behavior is discussed more extensively below. The overall pattern of decline of MCH conversion vs time shown in Fig. 1 are far less severe for the Re-containing catalyst than for the monometallic Pt catalyst. Although the effects of deactivation while in contact with hydrocarbon and restoration of activity by subsequent treatment with hydrogen are readily discernable for each catalyst, Fig. 1 shows that the presence of Re is associated with slower deactivation rates when exposed to hydrocarbon and more rapid activity recovery rates during exposure to pure hydrogen.

During the cyclic exposures to MCH followed by exposure to pure hydrogen, the PtRe catalyst also exhibits a significantly different pattern of individual product yields and selectivities as a function of time. This is evident from a comparison of Fig. 2 (for Pt/Al_2O_3) with Fig. 3 (for PtRe/Al_2O_3). During the first 20 h of exposure to MCH, toluene yield and selectivity rise to a maximum after several hours with the Pt catalyst and then fall. For the PtRe catalyst, however, the toluene yield and selectivity rise essentially monotonically during the first 20 h. Although benzene selectivity and yield fall monotonically during this period of both catalysts, these decreases are less rapid for the PtRe catalyst. The rise in toluene yields can be associated in part with the fall in benzene yields during the first 20 h but the trade-off is not complete as a close inspection of Figs. 2 and 3 will reveal; the net yield of total aromatics (benzene + toluene) falls during the first 20 h as shown by Fig. 4.

The data points plotted as C_6-products were computed by difference by mass balance and carbon balance. The make up of this fraction was also investigated semiquantitatively by gas chromatography. These C_6-compounds were predominantly

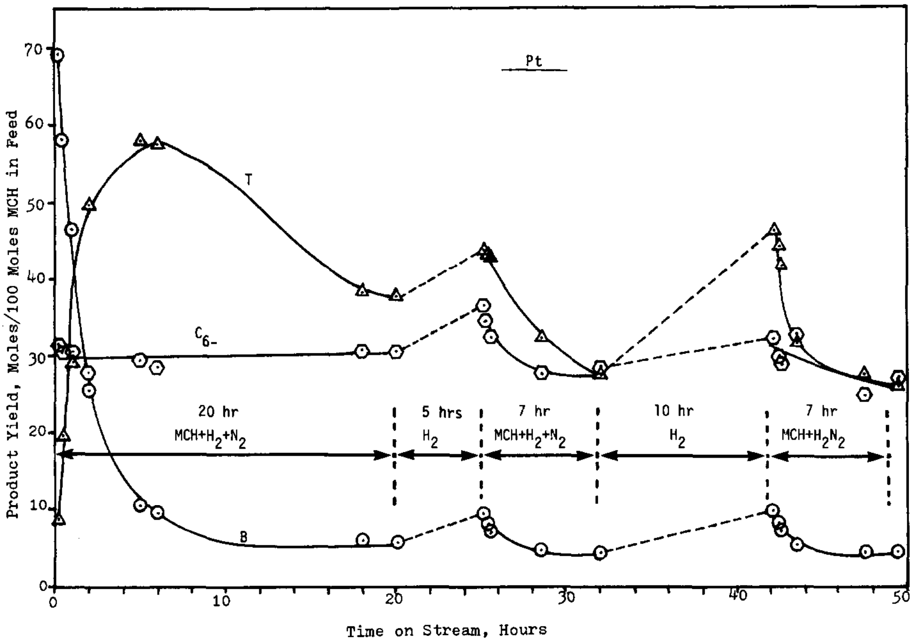

FIG. 2. Product yields vs time for Pt catalyst. (⊙) Benzene, (△) toluene, (⬡) moles MCH converted to C_6 (—) catalysts on hydrocarbon feed, (----) pure H_2 feed. Other conditions as in Fig. 1.

methane and ethane. In addition, traces of the following compounds began to be detected after about 8 h: 1-methylcyclohexene, 3-methylcyclohexene, and 1-methylcyclohexa-1-3-diene. No *n*-hexane or dibranched pentanes were detected in the products; we did not check for C_5-ring compounds in these experiments, although we did for sulfided catalysts (Part II) and detected none.

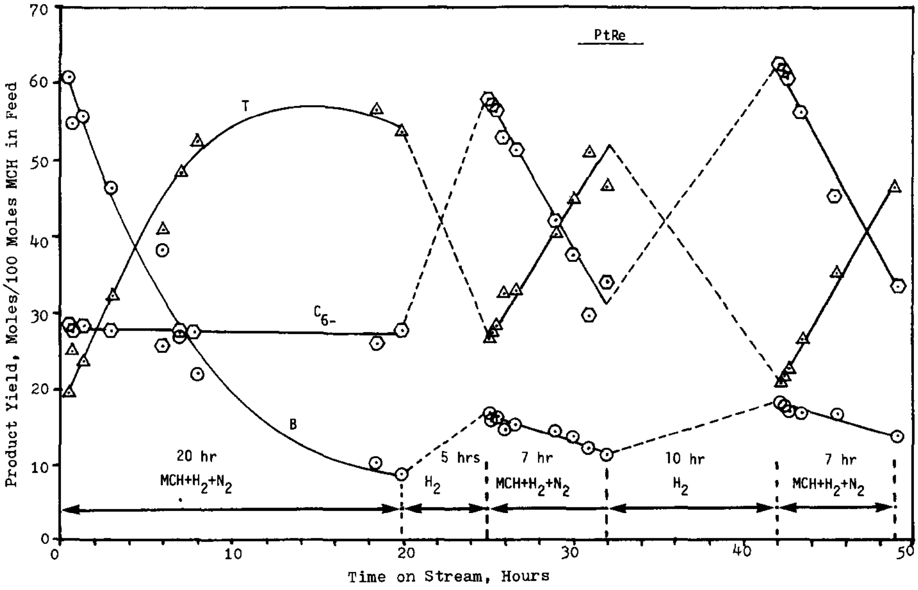

FIG. 3. Product yields vs time for PtRe catalyst. All symbols and conditions as in Fig. 2.

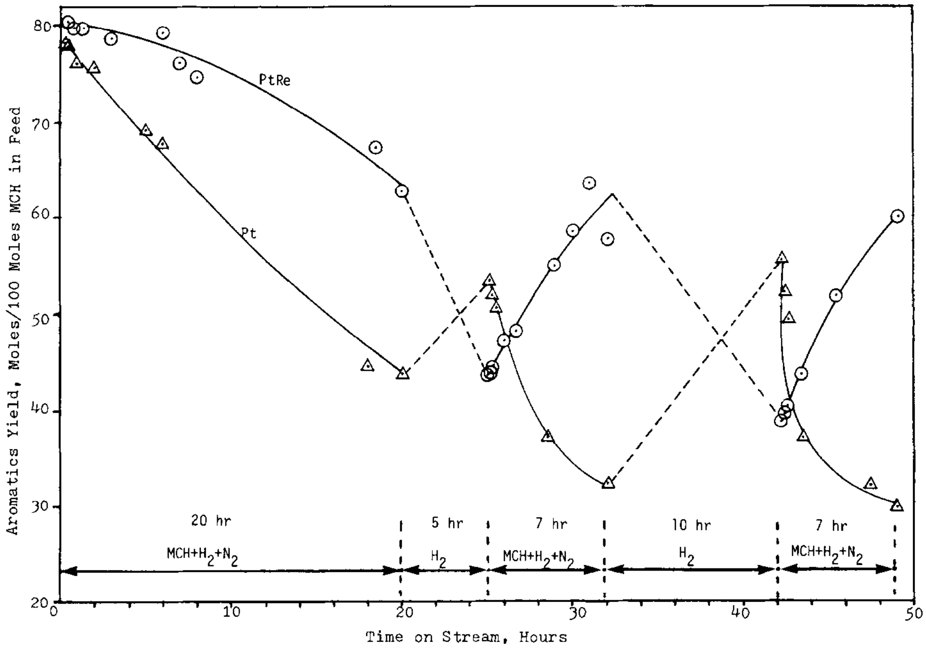

FIG. 4. Aromatic yields vs time. All symbols and conditions as in Fig. 1.

During the first several hours of reaction of MCH over the Pt catalyst, toluene yields and selectivities rise rapidly and those for benzene fall rapidly, presumably owing to selective deactivation of cracking sites. Demethylation is suppressed on the partially deactivated catalysts. The fact that selectivity and yield of C$_6$-products remain relatively constant during this period suggests that the phenomenon is complex and may involve activation of dehydrogenation sites. This type of behavior is also evident for the PtRe catalysts where it persists for the entire first 20-h period of exposure to MCH (Fig. 3). For the Pt catalyst, however (Fig. 2), the behavior during about the second 10 h appears to be one of deactivation of dehydrogenation because during this period toluene yield falls and C$_6$-yield remains about constant. In both cases total aromatic yield follows the behavior of total overall conversion during the first 20 h.

Because cracking reactions can take place at acidic sites of the support as well as at metallic sites, a few experiments were performed in which the catalysts had been preneutralized by contacting them with a solution of 0.05% NaOH following the procedure of Davis (*23*). The results obtained with the neutralized catalysts may be summarized as follows. For monometallic Pt the neutralized catalysts gave only slightly lower yields of C$_6$, the yields of benzene were about the same and the yields of toluene were significantly higher, especially during the first few and the last several hours of the 20-h period investigated. For neutralized PtRe the C$_6$-yields were substantially lower (<20%) throughout the 20-h period, the toluene yields were substantially higher throughout the period rising monotonically and approaching 80% at 20 h, and the benzene yields were substantially lower (i.e., 20–30%) during the first few hours and fell steadily to about 10% after 20 h. The implication for the present discussion is that after neutralization of the acidic sites substantial cracking activity remained, thereby indicating the important role of the metallic function in cracking. Beyond that, however, these results suggest also a strong interaction between the

Re and the acid sites, perhaps via a dual-site mechanism, and such interaction deserves further investigation. It may be related to the interactions between Re and the support which have been noted by others (*5–8*).

Switching off the hydrocarbon from t = 20 h to t = 25 h has remarkably different effects on the two different kinds of catalysts. Most notable is the slight increase in selectivity and yield for toluene with the Pt catalyst in contrast to a very sharp decrease in the case of the PtRe catalyst. The cracking activity (to C_6-products) of the PtRe catalyst is also greatly increased initially by this 5-h treatment in pure H_2 whereas that for the Pt catalyst is affected far less. It appears then that the hydrogen treatment restores cracking sites and deactivates sites for dehydroaromatization (see Fig. 4) in the PtRe catalyst whereas a similar H_2 treatment of the Pt catalyst restores dehydroaromatization sites but affects cracking sites very little.

As will be shown below less coke deposits, and deposits more slowly, on the PtRe catalyst during the first 20 h of exposure to MCH. During the subseuqnet 5 h of exposure to pure hydrogen coke is removed from both catalysts. The coke deposit may at first activate dehydroaromatization sites and deactivate cracking sites on both catalysts. The coke deposited later has a different effect on the Pt catalyst, viz. deactivation of dehydroaromatization but only a very small influence on cracking.

It appears that for both Pt and PtRe catalysts there is an activation period for toluene formation during the first few hours of exposure to MCH. This may be attributed to the early accumulation of a carbonaceous overlayer which promotes the catalytic reaction, in accordance with the recently published work of Davis *et al.* (*18*) for single crystals of Pt. After several hours of exposure to MCH the toluene yield and selectivity fall for the Pt catalyst but not for the PtRe catalyst. This behavior can be interpreted as arising from the formation of site-blocking graphitic deposits on the Pt catalyst. The hydrocracking activity of the Re may be thought to prevent or retard such deposition, at least in part, by the continuous hydrogenolysis of the precursors of such site-blocking graphitic deposits. The Re may also interfere with the reorganization of the hydrocarbonaceous overlayer to form graphitic-type deposits. The subsequent treatments in pure hydrogen remove "coke" from both types of catalysts. The greatly enhanced hydrocracking activity of the hydrogen-treated PtRe catalysts may be attributed to removal of the favorable catalytic carbon deposits which when present facilitate desorption of toluene products. Another interpretation might be based on activation of hydrogenolysis sites on PtRe by selective hydrogenolytic removal of carbonaceous deposits which poison these sites. In considering how hydrogenation activates hydrogenolysis sites on PtRe far more than on Pt, consideration should be give also to the viewpoint and evidence (*10, 11*) that Pt ensembles are necessary for hydrogenolysis but can be disrupted by alloying with Re. Perhaps exposure to hydrocarbon causes surface enrichment of alloy crystallites in Re with exposure to pure hydrogen reversing this process.

A second treatment with pure H_2 [from t = 32 h to t = 42 h] seems to produce very similar effects on the two catalysts as revealed by the product distributions when the MCH is switched on again after t = 42 h. Particularly noteworthy is that treatment in pure H_2 *lowers* the yield and selectivity for toluene and total aromatics over the PtRe catalyst whereas it *raises* these favorable properties for the Pt catalyst. Nevertheless, after switching the MCH back on stream this trend reverses: toluene (and total aromatics) production increases as coke redeposits on the PtRe catalyst but the trend is opposite for the Pt catalyst as it accumulates coke. The result is that only about 5 h after switching on the MCH, the PtRe catalyst begins to surpass the Pt cata-

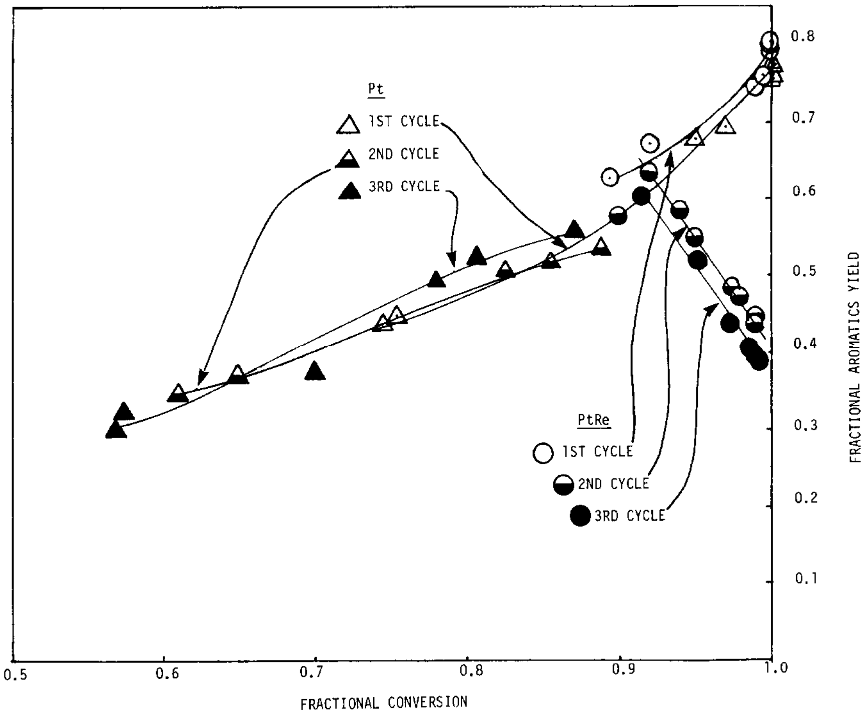

FIG. 5. Aromatics yields vs conversion (○) PtRe catalyst, (△) Pt catalyst. All conditions as in Fig. 1.

lyst in yield and selectivity for toluene and total aromatics.

A perhaps more instructive way to display the different yield data is by plotting yield against conversion, as shown in Fig. 5. In Fig. 5 the better catalyst gives data closer to the upper right-hand corner and the superiority of the PtRe over the Pt catalyst is again borne out in this figure, especially after the first cycle and some coke deposition has occurred. Figure 5 shows a striking change in the relationship between conversion and total aromatics yield after hydrogen treatment of the deactivated PtRe catalyst. Hydrogen treatment of the Pt catalysts does not produce any substantial change in this relationship.

Deposition of coke on the catalysts during sequential exposure to MCH + H_2 followed by pure H_2 was followed gravimetrically. The experiments were identical to those which gave the results discussed above, except they were done in a TGA apparatus with small samples of the catalysts. The amount of coke deposited is plotted versus time in Fig. 6. From these graphs it is evident that in every case of exposure to the MCH + H_2 mixture, the PtRe accumulated less coke owing to a suppression of coke formation during the earliest stages of exposure. The experiments of Fig. 6 were extended further than shown, viz. another exposure to pure hydrogen from 32 to 42 h followed by exposure to the MCH reactant from 42 to 49 h. The results showed no significant differences from the cyclic exposure from 20 to 32 h shown in Fig. 6. In a recent publication (*27*) Carter *et al.* state that during naphtha reforming the rate of coke formation is not significantly affected by the presence of Re in contrast to the influence of Ir in a bimetallic Pt catalyst. The contrast between this statement and the present results may reside in the fact we used pure MCH rather than a naphtha. It does not seem to be attributable to the cata-

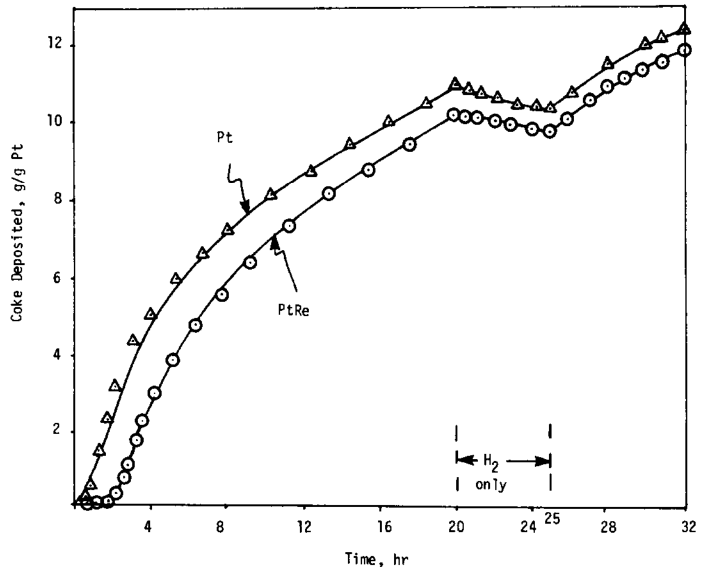

FIG. 6. TGA experiments: weight gain during 30-h exposure to hydrocarbon feed. (△) 0.35% Pt + 0.88% Cl/Al_2O_3, (⊙) 0.32% Pt + 0.325% Re + 0.88% Cl/Al_2O_3, initial masses: 85.63 mg of Pt cat; 86.37 mg of PtRe cat. 500°C, 1 atm, WHSV = 3 g MCH/g cat-h. Mole fraction of MCH was 0.05 in a carrier gas which was equimolar in H_2 and N_2.

lys presulfiding done by Carter *et al.* because we found that coke deposition was very greatly retarded on presulfided PtRe catalysts as reported in the subsequent paper (Part II).

Upon first exposure to MCH + H_2 there was a distinct lag in the weight gain for the PtRe—it appeared to gain no weight for almost the first 2 h—in contrast to the Pt catalyst which exhibited a measurable weight gain during the first several minutes. This behavior in MCH + H_2 is quite different from that observed (1) for mixtures of MCH + N_2. In the latter case the Re-containing catalyst appeared to gain weight slightly faster than the Pt catalyst but both catalysts gained weight more rapidly in MCH + N_2 than in the MCH + H_2 environment. It is, of course, well known that the presence of hydrogen suppresses coke formation but the present results also show that Re plays an important role in coke suppression in the presence of hydrogen.

It is not clear from Fig. 6 whether the presence of Re also accelerates coke removal during the periods the catalysts were exposed to pure H_2; weight loss due to coke hydrogenation takes place with both Pt and PtRe catalysts but does not seem to be faster with the bimetallic catalyst. It might be hypothesized that Re might maintain metal sites free of coke by continuous hydrogenation of the coke or its precursors during the periods of exposure to H_2 + MCH but the effect could be too small to observe gravimetrically as in Fig. 6. Judging from the earlier figures showing yields, sites for cracking are more susceptible to any cleaning action of Re than are sites for dehydroaromatization, at least in pure hydrogen. When MCH is also present, however, this trend appears to reverse with the result that the cracking sites are deactivated in the presence of MCH and Re. The last two sentences are based on the product-distribution results discussed above. The presence of Re may permit coke to preferentially deactivate cracking sites and also appears to catalyze the reactivation of these sites by treatment in pure H_2. The effect seems to be opposite on sites for dehydroaromatization. Without Re the influence of coke on the dehydroaromatization sites appears to be strongly opposite but the influence of coke on cracking sites appears to be substantially less.

The deactivation of cracking by coke deposition may be strongly related to the similar influence of small extents of surface sulfiding (*13, 15*): both appear to suppress cracking. In the present case the purity of the MCH (less than 0.2 ppm S) ensured that the effects were not due to sulfur. Sulfur may well be more important in industrial practice (*15*), however, where much higher partial pressures of H_2 would be expected to keep coke deposition rates low. In such cases a long period of time may be required before sufficient coke accumulates to effectively suppess cracking with the PtRe catalysts; selective presulfiding could then suppress hydrocracking early in the life of the catalyst. The accompanying paper gives results related to the effects of coke and sulfur using the same catalysts.

The present results for commercial, highly dispersed reforming catalysts suggest key roles of carbonaceous deposits as site-blocking poisons and perhaps as catalytic promoters. The results appear to be reasonably consistent with the observations and interpretations advanced by Somerjai and co-workers (*17, 18*) from experiments with low surface area, single-crystal metal catalysts at low pressures. The carbon overlayer that forms during the first few hours of exposure to MCH promotes the formation of toluene and deactivates hydrogenolysis sites. It is highly questionable whether the tiny crystallites of highly dispersed metal of the industrial catalysts used here may be envisioned to have terrace and edge topologies such as obtained by carefully cutting (*17, 18*) single crystals to expose high-index planes. For purpose of discussion we retain the terminology of terrace and edge sites but caution that for our highly dispersed catalysts it is more reasonable to think of a metal atom in a "terrace" as a surface atom of higher coordination number as compared to a surface atom of lower coordination number which might roughly correspond to an edge atom. Accordingly, the carbonaceous layer at first preferentially blocks low coordination atoms similar to kinked, edge sites shown by Blakely and Somerjai (*20*) to be hydrogenolysis sites. After several hours the carbonaceous deposits could increase or rearrange to the extent they begin to deactivate higher coordination or terrace type sites shown (*29*) to be the sites of dehydrogenation. The presence of Re might then retard the deposition of carbon and/or its rearrangement to a graphitic structure on the terrace sites or higher coordination sites of Pt, thereby slowing the deactivation of the dehydrocyclization reaction. The gravimetric measurements show clearly that Re lowers the rate of carbon deposition during the earliest stages of exposure to MCH.

Hydrogen treatment of Re-containing catalysts dramatically restores hydrogenolysis activity but does not so affect monometallic Pt catalysts. Re may cause the selective hydrogenation of carbonaceous deposits from sites which cause hydrogenolysis but it is not entirely clear whether such sites are on Pt, on Re, on both Re and Pt, or on clusters of PtRe. The ability of Re to markedly affect the catalytic activity of Pt, the early deposition of carbonaceous material on Pt and the important role of this carbon suggests that Re is closely associated with the Pt. Earlier work (*1*) has shown that carbon is more readily burned off Re-containing catalysts by treatment with oxygen. The present results show that Re also affects carbon deposition in the earliest stages, perhaps by dehydrogenation. This makes evident a very close physical association of Re with carbonaceous deposits. This taken together with the close association of Pt and carbon deposits is further evidence for the close interaction of Pt and Re on these catalysts. On the other hand, Bertolacinni and Pellet (*24*) showed it was not necessary for Re to be on the same support as Pt in order to retard coke formation in their experiments. We have also used a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 catalyst and found quite similar behavior to that of a Pt/Re/alumina catalyst with respect to aromatic yield vs time for the first 20 h of exposure. Migration of Re between supports is a distinct possibility although Bertolacinni and Pellet reported their analyses indicated no migration had occurred. We did not test for such migration. Certainly additional study of these questions seems called for.

If we suppose that Re exerts its important influence by incorporation into Pt crystals, then it might be hypothesized from the present results that some Re at low coordination surface sites corresponding to kinked edges in larger crystals is very active for hydrogenolysis but is rapidly poisoned by carbonaceous deposits which can be removed by treatment in pure hydrogen. The Re at higher coordination surface sites corresponding to the crystalline terraces of large crystals, however, might be assumed to keep these dehydrogenation sites free of deactivating carbon deposits by hydrogenolysis by hydrocarbon precursors of the deposits or by interfering with rearrangement of nonpoisonous hydrocarbonaceous material into poisonous graphitic-type deposits. It is important to recognize that the discussion thus far has sought an interpretation in terms of results and reasoning based on experiments with single crystals of pure Pt (*17, 18*). The extension we make to PtRe catalysts is certainly open to question and it might be equally useful to interpret our results in terms of the experiments and views of Sachtler and co-workers (*10–11*) whereby alloying would reduce the ensemble effect by diluting the Pt and this would cause reduced carbon deposition and increased catalyst stability. An interpretation of the present results based on this ensemble model would require that pure hydrogen treatment affect the extent of alloying and this could therefore be viewed as a surface enrichment of the metal crystallites in Pt brought about by hydrogen chemisorption. A converse type of surface enrichment might occur when the catalysts were exposed to hydrocarbon. This type of model can explain the increased yields of toluene formation during the first 20 h as a blockage of Pt ensembles by carbon for the monometallic case or as surface enrichment of Re in the bimetallic crystals during exposure to hydrocarbon. But this model does not seem to accommodate the much greater cracking of PtRe (compared to Pt) after the second and subsequent treatments in pure hydrogen.

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