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# Comparison of Platinum and Platinum–Iridium Catalysts for Heptane Reforming at Different Pressures

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The role of iridium in an alumina-supported platinum–iridium bimetallic catalyst was studied by examining the activity/selectivity behavior of platinum, iridium, and platinum–iridium catalysts using *n*-heptane reforming as a test reaction at 135 and 790 kPa. The iridium component imparted superior dehydrocyclization activity and deactivation resistance to the bimetallic relative to platinum. There appeared to be considerable synergism between platinum and iridium which resulted in suppression of surface coke formation. However, the bimetallic, even when presulfided, exhibited an undesirable higher hydrogenolysis activity, particularly at higher pressure. Comparison of results for the bimetallic catalyst and a mechanical mixture of platinum and iridium catalysts provided indirect evidence for the existence of bimetallic clusters on the platinum–iridium catalyst. This study also demonstrated that catalyst comparisons made near atmospheric pressure are not good indicators of relative performance at commercial conditions.

## INTRODUCTION

Catalytic reforming is an important process for the production of high octane gasoline, aromatics, and hydrogen from naphtha. In essence, the process involves passing a low octane, generally paraffin-rich, blend of $C_6$ to $C_{11}$ hydrocarbons over a solid catalyst at 725–785°K and 800–3200 kPa in the presence of an excess of hydrogen. The term, "reforming reaction" actually encompasses a complex network of reactions, including dehydrogenation, cyclization, isomerization, and hydrocracking (*1*). The "heart" of the reforming process is the catalyst, thus most of the major improvements in process efficiency have been due to the development of improved catalysts. For many years the industry standard was a catalyst consisting of platinum more or less atomically dispersed on a high surface area, chlorinated $\gamma$-alumina. A second generation of reforming catalysts began roughly a decade ago with the introduction of bimetallic catalysts such as platinum–rhenium and platinum–iridium. In perhaps overly simplistic terms, these consist of the standard $Pt/Al_2O_3$ catalyst with a second metal sharing the surface. Because the addition of the second metal has often caused dramatic changes in behavior, there has been and continues to be considerable interest in determining both the role played by this "promoter" metal and the form in which it exists on the surface. Platinum–rhenium has been the most commercially successful of the bimetallics and, consequently, many investigations have been made (*2–6*), attempting to explain how the presence of Re, a poor catalyst by itself, imparts to Pt large improvements in selectivity maintenance.

In contrast to the attention given Pt/Re, relatively little has appeared in the open literature concerning Pt/Ir (*7–11*). In patents issued to Sinfelt *et al.* (*12*) and Sprulock *et al.* (*13*) an iridium-containing catalyst is claimed to have high activity for naphtha reforming and, indeed, Pt/Ir catalysts in commercial units have been reported to have higher activity than Pt catalysts. Using both Auger spectroscopy and model re-

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actions, Rasser *et al.* (*10*) studied the promoting effect of Ir on both unsupported Pt/Ir alloys and supported Pt/Ir catalysts. It was concluded that, even at high bulk Ir concentrations, the surface of a Pt/Ir alloy is Pt-rich, and this was cited as being consistent with the low-pressure model reaction experiments in which Pt/Ir catalysts exhibited Pt-like behavior. Ramaswamy *et al.* (*11*) also speculated that a Pt/Ir alloy formed on the surface of an alumina-supported Pt/Ir catalyst and compared the performance of Pt and Pt/Ir catalysts in model reactions at atmospheric pressure. It was suggested that "dilution" of Pt by Ir leads to a lower surface concentration of coke precursors on Pt/Ir and that this accounts for its lower deactivation rate. A somewhat similar idea was proposed by Biloen *et al.* (*2*) to account for the effect of Re in a Pt/Re catalyst.

The idea that the active site on a catalyst is a small bimetallic cluster or alloy crystallite has been advanced by Sinfelt *et al.* (*8, 14, 15*) and other investigators (*3, 9*). This is one of two major topics which this experimental study addressed. The other major purpose of the research was to determine the effect of pressure on the relative performance of Pt/Ir and Pt catalysts, and, more specifically, to determine whether comparisons at atmospheric pressure involving these two catalysts have any relevance at commercial operating conditions.

## EXPERIMENTAL

*Apparatus.* The tubular reactor used in these studies was constructed from a 10 × 1.27-cm-o.d. piece of stainless-steel tubing and attached by tube fittings to a 150 cm length of 0.63-cm tubing shaped into a helix that served as a feed preheater as shown in Fig. 1. The reactor was immersed in a fluidized sandbath which was used to control reaction temperature. Catalyst bed temperature was measured using a digital thermometer connected to an iron constantan thermocouple located in a 0.32-cm-o.d. thermowell centered inside the reactor and extending over the length of the bed. Accurate metering of *n*-heptane and hydrogen feed was achieved by using a Milton Roy Minipump and a Matheson mass flow controller, respectively. Reactor pressure was controlled by a Grove back pressure regulator. Product sampling was achieved by using a gas sampling valve connecting the reactor outlet to a Perkin–Elmer Sigma-3 gas chromatograph, which was used for product analysis. All sample lines and the sampling valve were heated to prevent condensation. A 245 × 0.32-cm column packed with 10% TCEP on 100 × 120 mesh Chromosorb PAW was used in a temperature-programmed mode to separate the product into the roughly 15 major components ob-

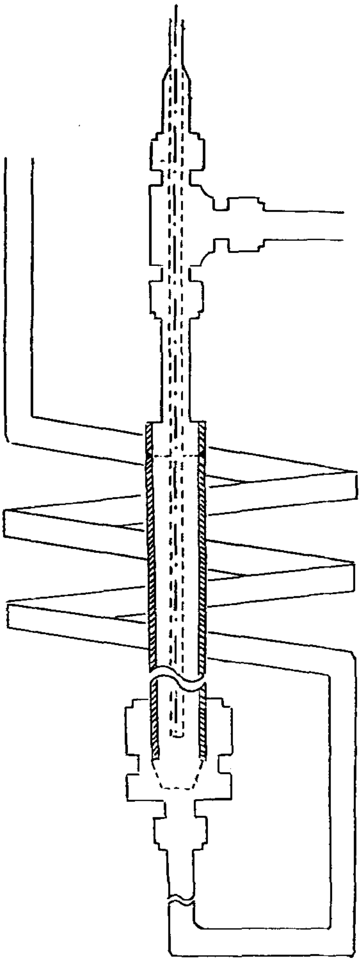

FIG. 1. Tubular microreactor.

served. Peak signals from the flame ionization detector were integrated using a Perkin–Elmer electronic integrator and recorded on a chart recorder. Peak identification was made by injecting a sample of the product into a GC/mass spectrometer. Peak response factors were determined by injecting known masses of each major pure component. Figure 2 is a schematic diagram of the apparatus.

*Materials.* Reagent grade *n*-heptane (>99.0%) was repeatedly filtered through alumina powder and 5A molecular sieves to remove impurities, notably, water and sulfur-containing species. This feed was maintained under dry nitrogen throughout each run. Hydrogen (99.99%) feed was passed through a deoxygenator and a molecular sieve drier prior to entering the reactor. In most cases, hydrogen sulfide (>99.5%) diluted with hydrogen was used for catalyst presulfiding. For two runs, a liquid mixture of 0.5 vol% thiophene in *n*-heptane was used in place of $H_2S$.

*Catalyst preparation.* Precalcined, high purity (>99.9%), high area (approx. 200 $m^2/g$) γ-alumina exturdates provided by American Cyanamid were sized to 20–30 mesh, then heated at 475°K for 5 hr in order to get a dry mass. Next, the dry support particles were immersed and agitated for 2 hr in a solution containing distilled/deionized water, hydrochloric acid, 0.05 *M* citric acid, and one or both of the following: dihydrogen hexachloroplatinate or dihydrogen hexachloroiridate.

The solution concentrations were chosen to give the desired mass % Cl, Pt, and/or Ir based on the dry mass of alumina used. Quantitative uptake of these species was confirmed by analysis of the residual solution. Citric acid was used as an impregnation aid because it has been shown (*16*) to promote a relatively uniform radial distribution for Pt in a $Pt/Al_2O_3$ catalyst by effectively competing with chloroplatinic acid for adsorption sites. It is a reasonable assumption that it affects Ir similarly. Following impregnation, the catalysts were heated in dry air for 1 hr at 615°K, a temperature

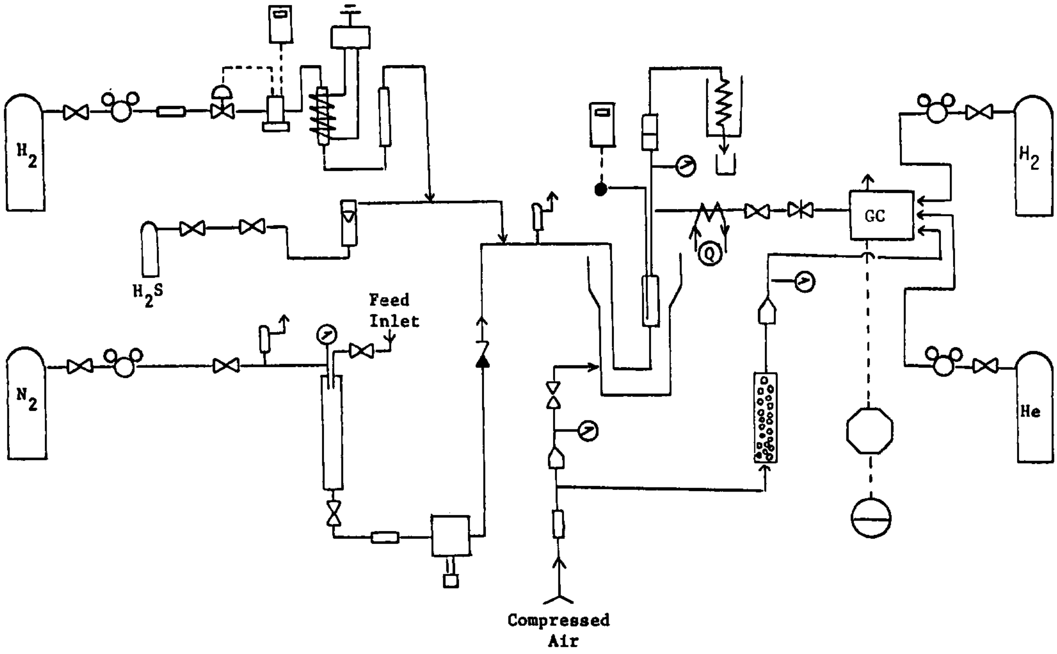

FIG. 2. Schematic flow diagram of experimental apparatus.

high enough to remove any traces of citric acid, yet low enough to avoid metal agglomeration.

The success of this procedure was confirmed in two ways. First, when Pt catalyst pellets were broken and tested with an indicator (2% KI in ethanol), which reveals the location of Pt (*17*), a uniform Pt distribution was found. Second, although facilities for chemisorption measurements were not available, the active metal dispersion was very high, as indicated by the fact that a Pt catalyst prepared as described above was found to be slightly more active for heptane reforming than a commercial catalyst with the same Pt and Cl levels.

*Testing procedure.* Typically, in commercial applications iridium-containing catalysts are sulfided prior to exposure to hydrocarbons at reforming conditions because the extremely high hydrogenolysis activity of unsulfided Ir can cause excessive cracking to light alkanes, particularly methane, and the resulting heat release can cause virtual "temperature runaway." The advisability of this practice was confirmed experimentally. Accordingly, all tests on iridium-containing catalysts involved presulfiding.

The standard start-up consisted of loading roughly 4 g of catalyst into the reactor, drying/reduction in flowing $H_2$ for 1 hr at 755°K and 790 kPa, leak testing at this condition, cooling to 615°K and presulfiding until $H_2S$ breakthrough was detected by lead acetate paper at the reactor outlet, "stripping" of excess $H_2S$ by flowing $H_2$ for 3 hr at 755°K, and, finally, introduction of *n*-heptane and hydrogen at the prescribed run conditions. All runs were made at 755°K with a 5 to 1 molar ratio of hydrogen to *n*-heptane. For runs made at 135 kPa a space velocity of 3.7 g heptane/g catalyst hr was used, while at 790 kPa, a value of 14.8 was used. The 135 and 790 kPa runs lasted 24 and 100 hr, respectively.

A test, in which no catalyst was used, was made at standard run conditions and no conversion of heptane was observed. This confirmed not only the absence of catalysis by the reactor walls, but also the absence of appreciable noncatalyzed gas phase reaction.

## DATA HANDLING AND DEFINITION OF TERMS

### *Kinetic Model*

Recognizing that a complex reaction network results, even when reforming a pure component feed such as *n*-heptane (*18*), it was obvious that a thorough kinetic investigation would be a major study in itself. Furthermore, because the emphasis was on the relative behavior of the catalysts, the reaction was merely a means of investigation and not an end in itself. Nevertheless, because the runs were conducted in a manner such that the conversion of heptane varied as deactivation occurred, a need existed for a rate expression adequate for calculation of a meaningful rate constant. Accordingly, a rate equation for the disappearance of *n*-heptane was obtained by conducting a limited kinetic study using a 0.6 mass% Pt catalyst at 790 kPa. It was impractical to study the kinetics at 135 kPa because of the relatively rapid deactivation at that pressure. The relation between heptane space velocity and fractional conversion was studied at 755°K with $H_2/C_7H_{16} = 5$ and the effect of hydrogen partial pressure was studied at constant heptane partial pressure. A plug flow performance equation was used to relate the conversion of heptane to the rate of disappearance of heptane. The assumption of plug flow behavior is sound because the reactor and particle sizes were chosen to satisfy the criteria specified by Rase (*19*) for achieving plug flow in a fixed bed, namely, $L/d_p \geq 50$ and $d_R/d_p \geq 10$, where $L$ = bed length, $d_p$ = particle diameter, and $d_R$ = reactor inside diameter.

Given that all of the catalyst test runs at a given pressure were conducted at nearly constant temperature, feed ratio, etc., and in a relatively narrow conversion range, it was deemed adequate to use a simple power law rate equation,

$$-r_{\mathrm{hep}} = k\,P_{\mathrm{hep}}^{\mathrm{a}} P_{\mathrm{H_2}}^{\mathrm{b}}, \qquad (1)$$

rather than attempt to determine all of the adsorption constants in a multiple Langmuir–Hinshelwood rate equation. Because of the large excess of hydrogen, volume change due to reaction was estimated to be negligible, as was the percentage change in hydrogen partial pressure across the reactor. With these simplifications and the data from the kinetic study runs, the following rate equation was found using the integral method (*20*):

$$-r_{\mathrm{hep}} = k\,P_{\mathrm{hep}}^{1.0} P_{\mathrm{H_2}}^{0.55}. \qquad (2)$$

The resulting integrated performance equation was,

$$k = \frac{\mathrm{WHSV}}{(\mathrm{MW})(P_{\mathrm{hep}})(P_{\mathrm{H_2}})^{0.55}} \ln\left(\frac{1}{1-x}\right), \qquad (3)$$

where WHSV = weight hourly space velocity, MW = molecular weight of heptane, and $x$ = fractional conversion. Fractional conversion on a molar basis for the reaction was calculated using a carbon atom balance equation,

$$X \equiv \frac{\text{total number of carbon atoms in the product, excluding heptane}}{\text{total number of carbon atoms in the product}}. \qquad (4)$$

With measured peak areas and predetermined response factors, a computer program was used to calculate the quantities appearing in this equation.

The activation energy was then determined using data taken by adjusting space velocity to give a constant conversion at 740, 755, 765, and 775°K. Using an Arrhenius plot, a value of 170 kJ/gmol was found. Considering the similarity between Pt and sulfided Ir, plus the narrow range of kinetic parameters used in the catalyst tests, it was felt that separate studies on Ir, Pt/Ir, etc., were not warranted.

Four measures of selectivity, each associated with a major reaction type, were used, as shown below.

| Reaction | Products |
|---|---|
| Aromatization | Toluene, benzene |
| Cyclization | Methylcyclohexane, dimethyl cyclopentanes |
| Hydrocracking/hydrogenolysis | Alkanes with <7 carbons |
| Isomerization | Iso-heptanes |

The selectivity for each reaction type was defined as the percentage of the number of moles of *n*-heptane actually converted that would be required to produce the measured number of moles of product of the appropriate type. These selectivity values, along with the rate constant normalized to 755°K, served as indices of performance in making catalyst comparisons.

It should be noted that many investigators prefer to lump cyclization and aromatization (as defined above) into a single term called dehydrocyclization. Cyclization and aromatization selectivity have been separately reported here because it is felt that this approach provides more information on relative catalyst behavior for the sequential reactions of cyclization and dehydrogenation (of the cyclic alkane).

### *Catalyst Labeling*

Table 1 lists the various catalysts tested and gives a shorthand label for each. In all cases the catalysts were supported on $\gamma$-alumina with 1.0 mass% Cl. Where different batches are indicated, identical procedures were used in the preparation.

## RESULTS AND DISCUSSION

The strategy employed in this work was to use a representative model reaction, i.e., *n*-heptane reforming, to study the behavior

TABLE 1

Catalyst Descriptions and Labels

| Catalyst No. | Description[a] |
|---|---|
| 3P-1 | 0.3% wt% Pt, first batch |
| 3I-11 | 0.3 wt% Ir, first batch, presulfided using thiophene |
| 6P-1 | 0.6 wt% Pt, first batch |
| 6P-2 | 0.6 wt% Pt, second batch |
| 3P3I-11 | 0.3 wt% Pt, 0.3 wt% Ir, first batch, presulfided using thiophene |
| 3P3I-22 | 0.3 wt% Pt, 0.3 wt% Ir, second batch, presulfided using $H_2S$ |
| 3P3I-12 | 0.3 wt% Pt, 0.3 wt% Ir, first batch, presulfided using $H_2S$ |
| MM-6P/6I-12 | Mechanical mixture of half 0.6 wt% Pt and half 0.6 wt% Ir, presulfided using $H_2S$ |

[a] All catalysts contained 1 wt% Cl.

TABLE 2

Comparison of Catalytic Activity

| Catalyst | Pressure (kPa) | Rate constant $k$, gmole/(hr · g cat. $kPa^{1.55}$), at 755°K | |
|---|---|---|---|
| | | Start of run[a] | End of run[b] |
| 3P-1 | 135 | 90 | 31 |
| 3I-11 | 135 | 77 | 24 |
| 6P-1 | 135 | 163 | 43 |
| 6P-2 | 135 | 166 | 43 |
| 3P3I-11 | 135 | 300 | 43 |
| 3P3I-22 | 135 | 212 | 44 |
| 3P3I-12 | 135 | 122 | 40 |
| 6P-2 | 790 | 55 | 24 |
| 3P3I-22 | 790 | 87 | 29 |
| MM-6P/6I-12 | 790 | 70 | 36 |

[a] One hour on stream.

[b] Twenty-four hours and a hundred hours on stream for 135 kPa runs and 790 kPa runs, respectively.

of Pt and Ir as separate components, as well as in combination, and to infer from the results the likelihood of interaction of Pt and Ir on the surface of a Pt/Ir catalyst. Because the surface was not directly observed, this approach could obviously yield only indirect information, but relative to more direct means of characterizing the surface, e.g., ESCA, this method had the advantage that the reaction itself "probed" the surface at realistic conditions.

### *Activity Comparisons at Low Pressure*

Table 2 summarizes the activity measurements for all runs made on the laboratory catalysts. The start-of-run rate constant values were measured 1 hr after introducing *n*-heptane. Although included for comparison purposes, these are of debatable significance for the Ir-containing catalysts because variations in presulfiding and subsequent "sulfur stripping" by $H_2$ during start-up caused radical variations in this quantity. For this reason comparisons will be based only on end-of-run activities, measured at 24 and 100 hr on stream for low- and high-pressure runs, respectively. Note that for the two runs made on separate batches of unsulfided 0.6% Pt catalyst excellent reproducibility was achieved for both initial and final activity. Figures 3 and 4 give a better illustration of the contrast in activity versus time behavior for Pt and Pt/Ir catalysts. The activity maximum observed at roughly 1 hr on stream for two low-pressure runs on Pt/Ir is believed to reflect competing effects: (i) rapid initial coking, which caused deactivation, and (ii) the reactive desorption of excess surface sulfur species by $H_2$, which "reactivated" temporarily poisoned sites.

*Platinum versus iridium.* Table 2 shows that the supported 0.3% Ir catalyst had an end-of-run activity that was only 77% of that for the 0.3% Pt catalyst. Given the equal metal loading and the nearly equal atomic masses for Pt and Ir, the two catalysts contained essentially the same number of metal atoms. Making the reasonable assumption that, at this low loading, nearly atomic dispersion was achieved in the impregnation, comparable numbers of sites should have existed initially on both catalysts. The more rapid decline in activity for the presulfided Ir catalyst thus indicates a

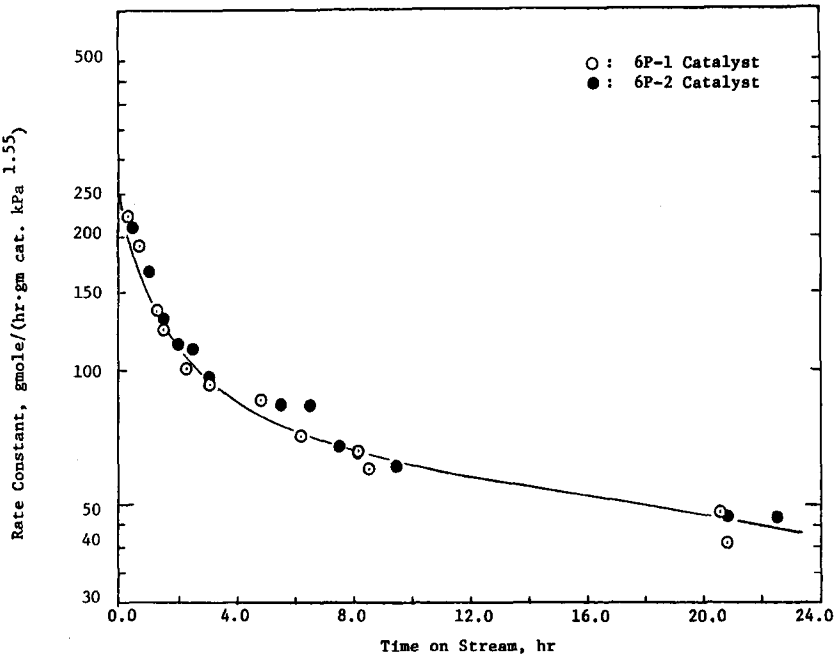

FIG. 3. Activity comparison between different batches of 0.6% Pt (6P) catalysts at 135 kPa.

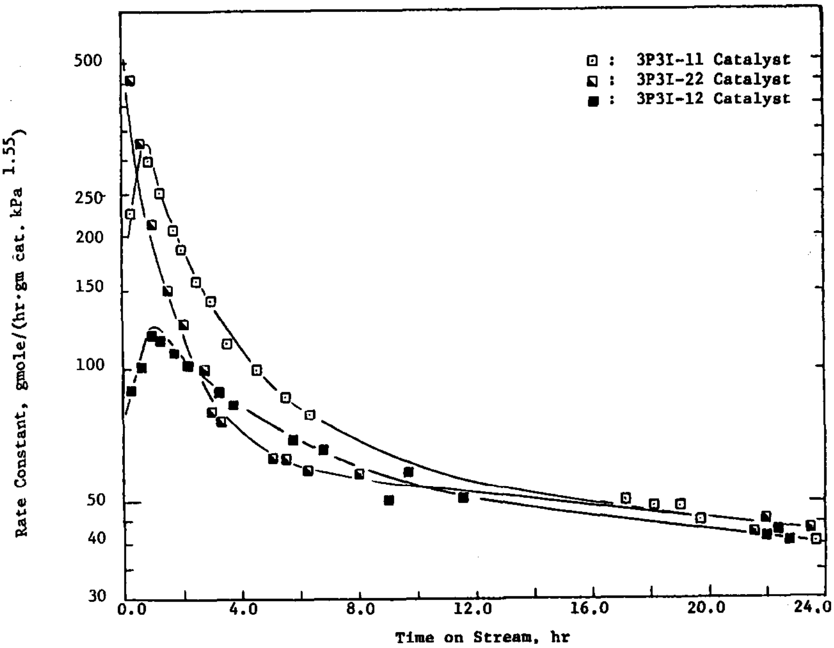

FIG. 4. Activity comparison among 0.3% Pt, 0.3% Ir (3P3I) bimetallic catalysts (different batches and different presulphiding methods) at 135 kPa.

greater vulnerability to deactivation by coke at low pressure. This may be attributed to the higher dehydrocyclization ability of Ir relative to Pt (see Table 3) causing a higher surface concentration of olefinic coke precursors, which polymerized at this low $H_2$ partial pressure.

*Platinum versus platinum–iridium.* It can be seen from Table 2 that the final activity for the two low-pressure 0.6% Pt runs was nearly the same as that for the three 0.3% Pt/0.3% Ir runs. If one thinks of these two catalysts as resulting from adding an increment of 0.3% Pt to the single metal 0.3% Pt and 0.3% Ir catalysts, respectively, it is clear that the impact of this increment of Pt was much more pronounced for the Pt/Ir case, considering that the single metal 0.3% Ir catalyst was measurably inferior to the 0.3% Pt catalysts. This is an indirect indication of some degree of interaction between Pt and Ir.

### *Activity Comparisons at High Pressure*

Table 2 also contains activity results for high-pressure runs on the 0.6% Pt catalyst, the 0.3% Ir/0.3% Pt catalyst, and a physical (mechanical) mixture of half 0.6% Pt and half 0.6% Ir catalysts. Close agreement between rate constant values for a given catalyst at low and high pressure should not be expected because, among other reasons, the low-pressure results were taken in a partial pressure range outside that used in developing the rate equation. However, at a given pressure relative activity comparisons are valid. With this in mind, the fact that at 790 kPa the Pt/Ir catalyst had a 20% higher activity than the Pt catalyst, while at 135 kPa the two catalysts were equal, is a clear indication that the bimetallic was more sensitive to pressure. It is also noteworthy that Fig. 5 shows that this activity advantage appeared to be increasing with time. Since the only difference between the two catalysts is the substitution of an increment of 0.3% Ir for 0.3% Pt, this greater resistance to deactivation was due to Ir or a Pt/Ir complex. At this higher pressure there was an adequate population of absorbed hydrogen near the metal sites to allow the superior hydrogenation ability of Ir or Pt/Ir to retard the growth of highly unsaturated hydrocarbon chains to a greater extent than Pt. Support for this assertion is provided by the selectivity results discussed later.

TABLE 3

Comparison of Selectivity for 0.3% Pt (3P-1), 0.6% Pt (6P), 0.3% Ir (3I-11), and 0.3% Pt/0.3% Ir (3P3I) Catalysts at 135 kPa with a 30% Overall Percentage Conversion[a]

System conditions
Temperature = 755° K
Pressure = 135 kPa
WHSV = 3.7 g/hr/g
Hydrogen/heptane = 5

| Catalyst | 3P-1 | 6P (avg.) | 3I-1 | 3P3I (avg.) |
|---|---|---|---|---|
| Aromatization selectivity (%) | 22.00 | 21.00 | 36.00 | 25.83 |
| Cyclization selectivity (%) | 14.50 | 16.00 | 5.50 | 13.33 |
| Hydrocracking selectivity (%) | 26.00 | 22.75 | 33.50 | 23.33 |
| Isomerization selectivity (%) | 37.50 | 40.25 | 25.00 | 37.50 |

[a] All values are reported with a 90% confidence interval of ±1.00%.

It should be pointed out that equipment limitations dictated 790 kPa as the "higher pressure" test condition, and commercial operation is typically at 1.5 to 3 times this pressure. Nevertheless, this test pressure was much closer to commercial conditions than the near-atmospheric pressure tests and it is reasonable to assume that the trends observed in going from 135 to 790 kPa can be extrapolated to actual reformer pressures. With this in mind, one might expect a substantial activity maintenance advantage for Pt/Ir relative to Pt in a commercial reforming reactor.

The activity results for the mechanical mixture of Pt and Ir catalysts are most informative. First, the activity for the mixture was 25% higher than for the Pt/Ir bimetallic catalyst. Note that the reactor contained the same quantity of Pt, Ir, Cl, and alumina in both cases and the only difference was the clear separation of Pt and Ir sites for the mixture. The performance dif-

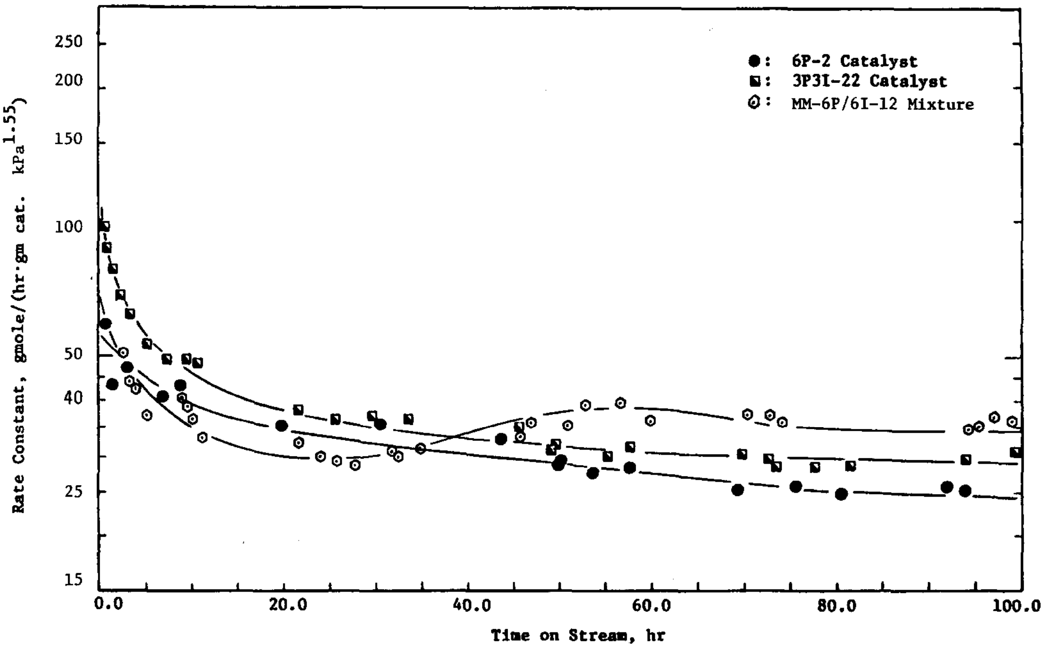

FIG. 5. Activity comparison among 0.6% Pt (6P-2), 0.3% Pt, 0.3% Ir (3P3I-22), and the mechanical mixture of half 0.6% Pt, half 0.6% Ir (MM-6P/6I-12) at 790 kPa.

ference thus points to a strong dependence of activity on the degree of association of Pt and Ir. Figure 5 shows that, unlike the Pt and Pt/Ir catalysts whose activity declined monotonically with time, the mixture of Pt and Ir catalysts showed an early run minimum during which it was less active than the other catalysts, but recovered considerable activity before lining out halfway through the run. The selectivity results reveal an explanation for this.

### *Selectivity Comparisons at Low Pressure*

*Platinum versus iridium.* In all runs the selectivity pattern changed rapidly during the first 10 hr, then remained nearly constant until the end of run; thus only the stable values are presented for comparison purposes in Table 3. This table shows that at low pressure Ir has a much greater ability than Pt to complete the sequence of cyclization and dehydrogenation necessary for aromatics formation. The higher value for aromatization selectivity is the most obvious evidence, but the lower cyclization selectivity also supports this. Note that cyclization selectivity as defined here is merely a measure of that fraction of converted heptane which emerged from the reactor as a cyclic alkane. Because such species are intermediates in the series reaction that forms aromatics, perhaps a more meaningful measure of cyclization ability is the sum of the selectivities for aromatization and cyclization. On this basis, iridium appears to have a superior ability to form cyclic alkanes, possibly because of a higher dehydrogenation activity which results in more rapid formation of olefinic species that later isomerize to ring compounds.

The higher hydrocracking selectivity for Ir relative to Pt was expected and indicates that, while the extreme hydrogenolysis activity of Ir had been suppressed by selective poisoning (by sulfur) of the most active sites, enough remained to cause a higher rate of carbon–carbon bond scission. The lower isomerization selectivity for Ir was merely a consequence of the large percentage of normal and iso-heptanes which were cracked prior to exiting from the reactor, and thus is not a meaningful indicator of relative isomerization ability.

*Platinum versus platinum–iridium.* At low pressure the bimetallic was somewhat more selective than Pt for aromatization and hydrocracking at a given conversion, as shown in Table 3. However, the Pt/Ir selectivity results were much closer to those of the Pt catalyst than to the average of the separate 0.3% Pt and 0.3% Ir selectivity values. It is tempting to assert that this implies that the active species is a Pt/Ir alloy consistent with the observation of Rasser *et al.* (*10*) that Pt/Ir alloys have a surface rich in Pt and that their behavior is Pt-like. However, in a complex reaction involving relatively stable intermediates, it may be argued that the lack of additivity for the effects of the Pt and Ir components was due to intermediates generated on an Ir site migrating to a nearby Pt site and vice versa, in somewhat the same way that Cl and Pt sites are believed to cooperate in the isomerization reaction (*21*). Although this latter possibility was considered unlikely to account for the observed behavior of Pt/Ir, a more convincing "proof" was needed. It is felt that the high-pressure selectivity data to be discussed later provide this.

Figure 6 for the Pt/Ir catalyst is representative of the selectivity versus time curves for the catalysts tested. Note that early in this low-pressure run aromatization declined rapidly from an initially very high value, while isomerization and cyclization increased. Hydrocracking selectivity was relatively constant. This agrees with the commonly accepted view that coke formation primarily affects the metal sites responsible for dehydrocyclization.

### Selectivity Comparisons at High Pressure

By comparing the low- and high-pressure selectivity data in Tables 3 and 4, respectively, it can be seen that for the 0.6% Pt and 0.3% Pt 0.3% Ir catalysts the most dramatic effect of increasing pressure was a decrease in cyclization with a corresponding increase in isomerization. Aromatiza-

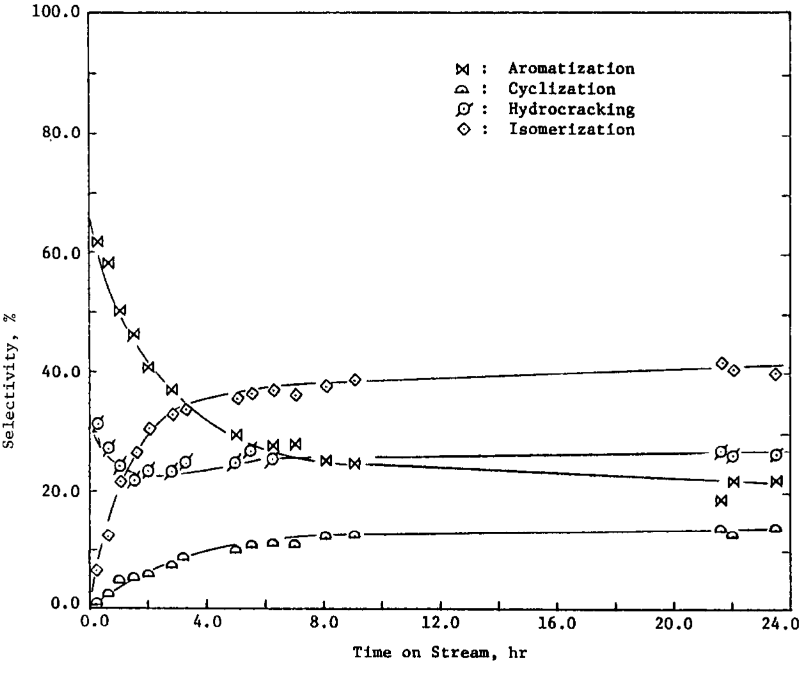

FIG. 6. The change of various selectivities with time on stream at 135 kPa, 0.3% Pt, 0.3% Ir catalyst (3P3I-22).

TABLE 4

Selectivity Comparisons between 0.6% Pt (6P-2) and 0.3% Pt, 0.3% Ir (3P3I-22) Catalysts at 790 kPa with an Overall Percentage Conversion of 60%[a]

| System conditions | | | |
|---|---|---|---|
| | | Temperature = 755°K<br>Pressure = 790 kPa<br>WHSV = 14.8 g/hr/g<br>Hydrogen/heptane = 5 | |
| Catalyst | 0.6% Pt (6P-2) | 0.3% Pt/0.3% Ir (3P3I-22) | Mechanical mixture half 0.6% Pt, half 0.6% Ir (MM-6P/6I-12) |
| Aromatization selectivity (%) | 17.5 | 19.5 | 19.6 |
| Cyclization selectivity (%) | 0.5 | 0.5 | 3.6 |
| Hydrocracking selectivity (%) | 22.5 | 28.5 | 38.0 |
| Isomerization selectivity (%) | 59.5 | 51.5 | 38.8 |

[a] All values are reported with a 90% confidence interval of ±1.00%.

tion also declined, while hydrocracking increased by a similar amount. Part of this difference is due to the fact that the data in the two tables are referenced to different conversions, but the main reason is the unfavorable effect of increased pressure on the equilibrium concentration of aromatics and naphthenes (*22*). Table 4 shows that at 790 kPa and 60% conversion Pt/Ir had higher aromatization and hydrocracking selectivities than Pt; but Table 5, which directly compares the difference between these two catalysts at low and high pressure, reveals that the aromatization advantage for Pt/Ir was less at higher pressure. Overall, the data indicate that, while increasing pressure improves Pt/Ir activity relative to Pt, this benefit is offset by a substantial increase in hydrocracking, which in a refinery might mean a lower liquid yield at a given product octane.

The final comparison afforded by Table 4 is that between the Pt/Ir catalyst and the mechanical mixture of Pt and Ir catalysts. Although presulfided in the same manner as the Pt/Ir catalysts, the mixture catalyst showed a remarkably higher hydrocracking selectivity and an unexpectedly high con-

TABLE 5

The Effect of Pressure on Relative Activity and Selectivity for Platinum (6P) and Platinum–Iridium (3P3I) Catalysts

| Items for comparison[a] | Low pressure[b] (135 kPa) | High pressure (790 kPa) |
|---|---|---|
| Relative activity[c] | 1.01 | 1.20 |
| Difference in aromatization selectivity[d] | 5.00 | 2.50 |
| Difference in cyclization selectivity[d] | −4.33 | −0.50 |
| Difference in hydrocracking selectivity[d] | 0.50 | 10.0 |
| Difference in isomerization selectivity[d] | −1.17 | −12.0 |

[a] All quantities are evaluated at the end of run, i.e., 24 and 100 hr for 135 and 790 kPa runs, respectively.

[b] Average values are reported for the low-pressure data.

[c] Relative activity is defined as $(k_{Pt/Ir})/(k_{Pt})$.

[d] (Selectivity of Pt/Ir) − (selectivity of Pt).

centration of cyclic alkanes in the product. Furthermore, Figs. 7 and 8 show that both aromatization and hydrocracking selectivity went through minimum values early in the run and later lined out at values much higher than for Pt/Ir. Comparing these figures with Fig. 5, it appears that the activity recovery for the mixture catalyst resulted from increased hydrocracking and stabilization of aromatization. This behavior can definitely be attributed to the Ir component of the mixture since the 0.6% Pt catalyst, also shown on these figures, experienced a continuous decline in both of these selectivities as well as in activity.

In summary, comparison of the Pt/Ir and mechanical mixture runs demonstrates that the separation distance between Pt and Ir sites has a large effect on catalytic behavior. For the mixture this distance was on the order of hundreds of microns, while for the bimetallic catalyst it would have been, at most, hundreds of Angstroms, and possibly zero if alloy clusters were formed. The odd behavior of the mixture can be best explained in terms of a gradual release of sulfur from isolated Ir sites. Apparently, relative to the Ir on a Pt/Ir catalysts, the Ir in the mixture had a lower binding strength for the Ir–S bond. If most of the Ir on a Pt/Ir catalyst also existed as an entity separate from Pt, albeit at a distance of only 10–100 Å, it is hard to rationalize how the presence of Pt could enhance the stability of preadsorbed sulfur on iridium since this would involve an electronic interaction. Such an interaction would require either direct alloying or at least a close-proximity "inductive effect," thus the results of this study support the hypothesis that much of the Pt and Ir on a Pt/Ir catalyst is present in bimetallic clusters. Obviously, only a more direct investigation of surface species can resolve the detailed nature of the Pt–Ir interaction. In addition, the mechanism by which Pt and Ir atoms might migrate to common surface locations during catalyst preparation or operation remains to be defined.

As to the means by which iridium "pro-

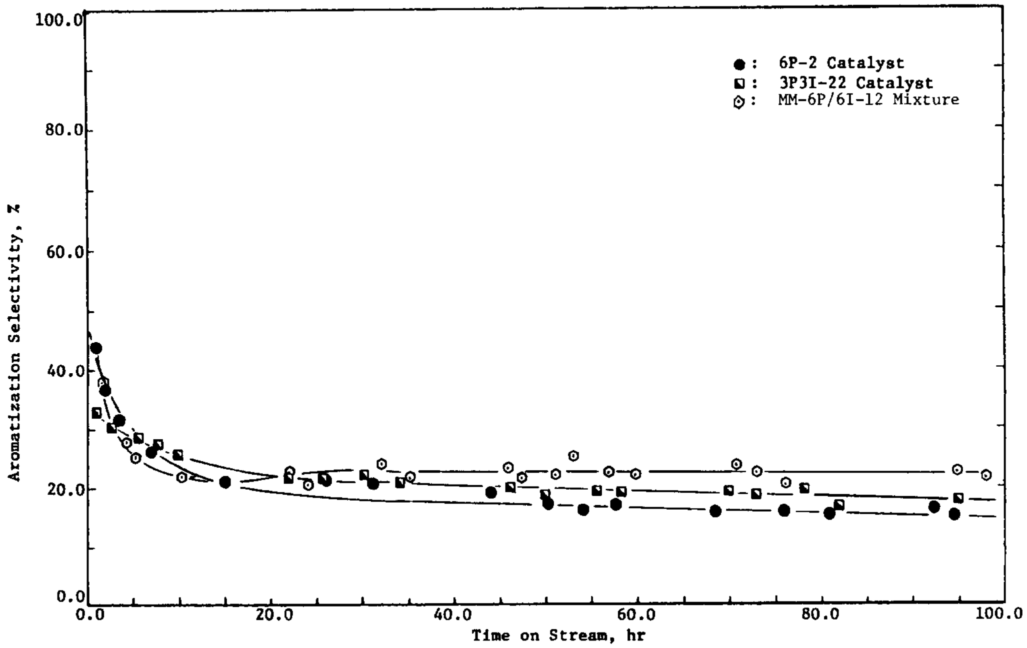

FIG. 7. Aromatization selectivity comparison among 0.6% Pt (6P-2), 0.3% Pt, 0.3% Pt, 0.3% Pt, 0.3 Ir (3P3I-22), and the mechanical mixture of half 0.6% Pt, half 0.6% Ir (MM-6P/6I-12), at 790 kPa.

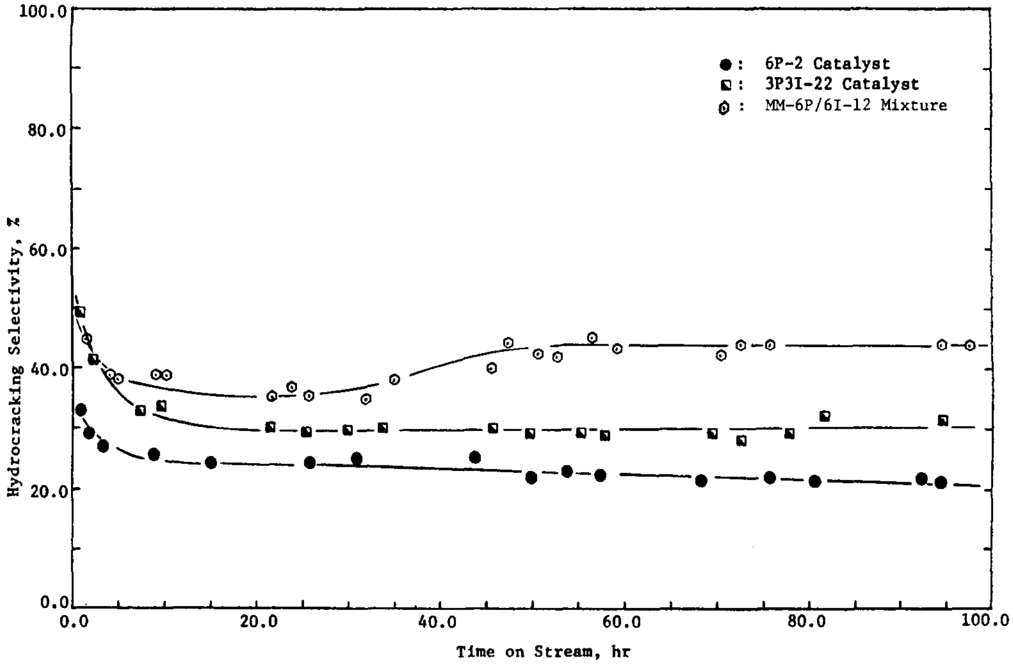

FIG. 8. Hydrocracking selectivity comparison among 0.6% Pt (6P-2), 0.3% Pt, 0.3% Ir (3P3I-22), and the mechanical mixture of half 0.6% Pt, half 0.6 Ir (MM-6P/6I-12), at 790 kPa.

motes" platinum, at least two possibilities, both involving bimetallic clusters, come to mind. First is the possibility that the incorporation of Ir into Pt to form an alloy cluster results in a crystallite with a composite electronic nature (band structure) that is more favorable for dehydrocyclization and coke suppression than that of comparably sized Pt or Ir single metal crystallites. This synergistic effect, while possibly due to the alloy having special geometric features, e.g., metal–metal bond distance, is more likely to be due to an electronic effect.

A second possibility is that in a bimetallic cluster the sulfided Ir "divides" the Pt into separate ensembles or domains consisting of small numbers of contiguous surface Pt atoms. It can be argued that this surface segregation effect of Ir on Pt would increase the resistance of the catalyst to coking since large platinum clusters have been postulated to be more susceptible to carbon build-up (*2*). This is essentially the explanation given by Biloen *et al.* (*2*) for the promoting effect of Re on Pt in a Pt/Re reforming catalyst. Rhenium and iridium differ significantly in chemical behavior, thus it is debatable whether a close similarity in their promotional mechanism with respect to Pt should be expected. Distinguishing between the two possible mechanisms just described will obviously require well-conceived experimentation. Surface characterization techniques such as infrared spectroscopy of adsorbed species, e.g., CO, might be useful in determining the extent of electronic interaction.

## CONCLUSIONS

(1) Iridium has a higher intrinsic activity for dehydrocyclization and hydrocracking than does platinum.

(2) At commercial reforming conditions, Pt/Ir catalysts have higher activity and better activity maintenance than Pt catalysts because synergism between Pt and Ir gives Pt/Ir a superior ability to hydrogenate coke precursors.

(3) Pt/Ir catalyst behavior is distinctly different from that of a mechanical mixture

of separate Pt and Ir catalysts and most of this difference can be attributed to a very close association between Pt and Ir in a Pt/Ir catalyst, perhaps even to the extent of bimetallic cluster formation.

(4) Atmospheric pressure tests of the relative activity/selectivity of Pt and Pt/Ir catalysts are not good indicators of relative behavior at commercial conditions.

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