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Model Compound Reforming Studies: A Comparison of Alumina-Supported Platinum and Iridium Catalysts

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Model compound reforming studies have been carried out over alumina-supported platinum and iridium catalysts. Cyclohexane and methylcyclopentane were selected to model the dehydrogenation and isomerization–dehydrogenation reactions, respectively, of naphthenes, while, *n*-heptane was chosen to model paraffin dehydrocyclization. Under typical reforming conditions, the conversion rates and selectivity patterns of these model compounds were found to be highly dependent upon the choice of metal. Platinum, for example, was found to be more active and selective for the aromatization of cyclohexane and methylcyclopentane than iridium. Iridium, in contrast, was observed to be a more active and selective *n*-heptane dehydrocyclization catalyst than platinum. Synthetic mixtures of model compounds were also investigated. These studies showed that paraffin dehydrocyclization is more strongly retarded by competitive adsorption processes than naphthene aromatization.

1. INTRODUCTION

Among refining processes, reforming capacity is second only to that of catalytic cracking. In view of this tremendous capacity, there are large incentives to operate reformers efficiently. Efficient operation requires a fundamental knowledge of how the catalyst and reaction variables affect product selectivity and component conversion rates.

The reforming of petroleum naphthas is carried out over bifunctional catalysts which consist of a single transition metal or a combination of metals dispersed on an acidic support such as alumina or silica–alumina (*1, 2*). At temperatures near 770 K, such catalysts simultaneously promote metal- and acid-catalyzed conversions of saturated hydrocarbons to aromatics. The major reactions promoted by bifunctional catalysts are hydrogenation, dehydrogenation, isomerization, cyclization, and hydrocracking (*3–5*). The effects of numerous process variables on the reforming of individual hydrocarbons, as well as whole naphtha feedstocks, over platinum catalysts are known in considerable detail (*6–11*). This understanding has steadily evolved since the introduction, by Universal Oil Products, of platinum reforming over 30 years ago (*12*). Compositional changes within a typical four-reactor-bed reformer operating at a severity of 101 research octane number are shown in Fig. 1. Naphthenes, alkylcyclopentanes, and alkylcyclohexanes, are shown to be readily converted within the first 40% of the four-reactor reformer train. The aromatization of naphthenic hydrocarbons is generally highly selective (*6*). Noncyclic paraffinic hydrocarbons, in contrast, are more difficult to aromatize. Their conversion continues throughout the entire reformer train. The production of aromatic molecules via the dehydrocyclization of paraffins is less selective than naphthene aromatization (*6*). The lower aromatic selectivities demonstrated by paraffins result primarily from competitive isomerization and hydrocracking reactions (*1, 5*).

On the basis of these different conversion rates and selectivities, cyclohexane and methylcyclopentane were selected to

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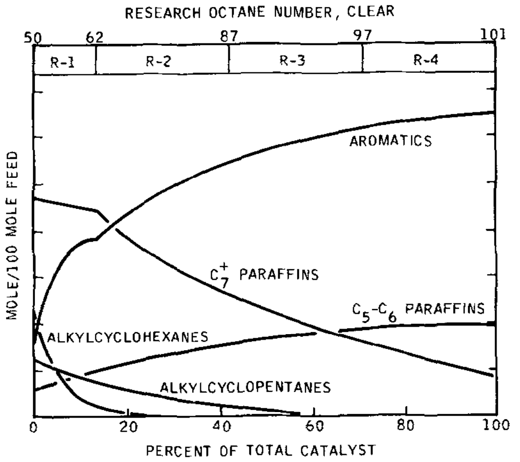

FIG. 1. Typical reformer composition profiles. Conditions: 0.3% Pt-Al_2O_3, 1725 kPa, H_2/feed = 3.3, 0.9% Cl.

model the dehydrogenation and isomerization–dehydrogenation reactions, respectively, of naphthenes, while, *n*-heptane was chosen to model paraffin dehydrocyclization. A major goal of these studies was to gain a better understanding of how metals influence the conversion patterns of naphthenic and paraffinic hydrocarbons. Metal specificity was investigated using alumina-supported platinum and iridium catalysts. Catalyst acidities were maintained as similar as possible by employing comparable chloride concentrations on the alumina supports.

2. EXPERIMENTAL METHODS

Catalysts

The platinum and iridium catalysts employed in these studies were supported on γ-Al_2O_3 carriers. The γ-Al_2O_3 carriers exhibited BET surface areas in the range of 180–190 m^2/g and were indistinguishable by X-ray diffraction measurements.

The 0.3% platinum–alumina was obtained from American Cyanamid. The catalyst, as received, contained 0.30% platinum and 0.55% chlorine (*14*). Before use, the catalyst was calcined at 773 K under 20% O_2/He (500 cm^3/min) for 4 hr.

The 0.3% iridium–alumina was prepared by the incipient wetness impregnation of γ-Al_2O_3 (supplied by Engelhard) with an aqueous solution of chloroiridic acid containing added HCl. The impregnate was dried at 393 K for 16 hr under air and then mildly calcined at 543 K under 20% O_2/He (500 cm^3/min) for 4 hr. The calcined catalyst contained 0.302% iridium and 0.59% chlorine (*14*).

Chloride adjustments to the above catalysts were made by the use of standardized aqueous HCl solutions. At a given chloride concentration the acidities, as measured by *n*-butylamine adsorption, of the starting platinum and iridium on alumina catalysts are comparable.

Chemisorption Measurements

Hydrogen and carbon monoxide chemisorption studies were performed with a conventional glass vacuum system (*15*). Ultimate dynamic vacuums of approximately 10^{-7} Torr were obtainable. Pressure measurements were made with a Texas Instruments precision pressure gauge. Samples of 3 to 4 g, sieved to 20–40 mesh size, were placed in flow-through cells made of Vycor. All samples were reduced *in situ* at 773 K under hydrogen (500 cm^3/min) for 2 hr. The reduced samples were cooled to 723 K under hydrogen and evacuated at this temperature for 0.5 hr. The samples were then cooled under dynamic vacuum to room temperature (298 K). Longer reduction and evacuation times did not measurably affect the subsequent chemisorption results.

Hydrogen and carbon monoxide uptakes were determined at 298 ± 2 K on the reduced and evacuated samples. Typically, 0.5 hr was allowed for each uptake point. H(total)/M ratios were calculated by assuming that hydrogen uptake extrapolated to zero pressure corresponds to saturation coverage of the metal. Total hydrogen uptake was determined by extrapolation of the high-pressure linear portion of the isotherm as described by Benson and Boudart (*16*) and Wilson and Hall (*17*). A second isotherm was measured after evacuating

(10^{-5} Torr) the sample following the initial isotherm at 298 K for 0.17 hr. The difference between these two isotherms at zero pressure gave the amount of hydrogen irreversibly absorbed by the catalysts at room temperature. CO/M ratios were calculated by determining the carbon monoxide uptakes on the reduced and evacuated samples and assuming that this quantity represented the sum of carbon monoxide weakly bound to the alumina support and strongly bound to the metal. The sample was then evacuated (10^{-5} Torr) for 0.17 hr at room temperature and a second isotherm measured. Since the second isotherm measured only the carbon monoxide weakly adsorbed on the support, subtraction of the two isotherms gave the quantity of carbon monoxide strongly associated with the metal component. In accordance with previous studies, the amount of strongly bound carbon monoxide at 100 Torr was chosen as saturation coverage of the metal (*18*).

Catalytic Conversions

Hydrocarbon conversion reactions were carried out in a 25-cm^3, stainless-steel, fixed-bed, isothermal hydrotreating unit operated in a single pass mode. The reactor was heated by a fluidized sand bath. Hydrogen was passed through Deoxo and molecular sieve drying units prior to use. Feed was delivered by a dual-barrel Ruska pump which allowed continuous operation.

Cyclohexane dehydrogenation studies were performed at 573 K under 101 kPa (760 Torr) total pressure. A space velocity of 1130 WHW was utilized and the hydrogen/cyclohexane mole ratio was maintained at 2.3. Standard Koros–Nowak tests indicated that under these conditions no detrimental transport influences were operating (*19*). Prior to introduction of feed the catalysts were reduced *in situ* with hydrogen (500 cm^3/min) at 773 K for 2 hr. The extent of cyclohexane dehydrogenation was followed by on-line GC measurements.

Methylcyclopentane aromatization investigations were carried out at 723 to 798 K under either 690 or 1380 kPa total pressure. A space velocity of 40 WHW was used and the hydrogen/methylcyclopentane mole ratio was held at 5.0. Catalysts were reduced *in situ* under 1380 kPa hydrogen (1100 cm^3/min) at 773 K for a minimum of 2 hr. The reduced catalysts were subsequently sulfided in place at 101 kPa using a dilute H_2S/H_2 mixture at the preselected reaction temperature. Sulfiding was continued until breakthrough H_2S was detected in the exit gas. Feed was introduced at the reaction temperature to minimize sulfur loss from the catalysts. Feed sulfur level adjustments were made by the addition of standardized thiophene solutions. All reaction products were analyzed by on-line GC measurements. The product train was equipped with a gas-phase sparger to ensure product homogenization. A 30-ft × $\frac{1}{8}$-in. (o.d.) stainless-steel column packed with 20% SP-2100 on a ceramic support allowed complete product separation and identification. Detection was by flame ionization.

n-Heptane dehydrocyclization experiments were carried out at 698 to 783 K under either 690 or 1380 kPa total pressure. Catalysts were reduced *in situ* at 773 K under 1380 kPa hydrogen (1100 cm^3/min) for 2 to 16 hr. When sulfur-containing feeds were employed, prereduced catalysts were sulfided with a dilute H_2S/H_2 mixture to breakthrough. *n*-Heptane sulfur levels were adjusted by the addition of standardized thiophene solutions. Feed was introduced at 673 K and over a 24-hr period the reaction temperature was slowly increased to the desired setting. This procedure was found to give highly reproducible reaction patterns. Space velocities were varied between 20 and 275 WHW. The hydrogen/*n*-heptane mole ratio was maintained at 5.0 throughout the studies. Direct analyses of all reaction products were made by on-line GC measurements similar to those described above.

Catalysts recovered from the various model compound conversion reactions were routinely analyzed for carbon and chlorine content (*14*).

Reaction rates for the various hydrocarbon conversion reactions were calculated using the expression

$$\text{rate} = \frac{F \Delta X}{W},$$

where F is the hydrocarbon feed rate in moles per hour, W is the weight of the catalyst in grams, and ΔX is the extent of conversion for a particular reaction. Although this equation is strictly valid for differential conversions (<10%) only, plots of methylcyclopentane and *n*-heptane conversion against reciprocal space velocity were linear up to about 70% conversion. The use of the above expression for comparative purposes was, therefore, judged to adequately describe these systems over a wide range of conversions.

3. RESULTS AND DISCUSSION

A. Catalyst Characterization

The chemisorption properties of the platinum and iridium catalysts employed in these studies are summarized in Table 1. Hydrogen and carbon monoxide uptakes are expressed in terms of adsorbate/metal ratios. The use of adsorbate/metal ratios to characterize these catalysts instead of average crystallite sizes or percentage dispersion was chosen since assumptions involving surface coverage and adsorption stoichiometries were not requires (*20*). In agreement with numerous reported studies, the 0.3% platinum catalyst exhibited H(total)/M and CO(irrev)/M ratios near unity (*20–24*). The 0.3% iridium catalyst, in contrast, displayed irreversible adsorbate/metal ratios approaching a limiting value of 2. The high hydrogen uptakes have been shown to be a property of highly dispersed iridium particles and are not a consequence of hydrogen spillover (*25*). Both starting catalysts were devoid of metal or metal oxide X-ray diffraction patterns. The absence of such patterns indicates that the supported metal crystallites are less than 5.0 nm in diameter (*26*). TEM examination of the platinum catalyst revealed the presence of a number of 1.0- to 1.5-nm crystallites. No metal particles were detected in the iridium catalyst by high-resolution TEM. On the basis of the resolution of the TEM, this places an upper limit of 0.6 nm on the diameter of the iridium particles (*25*). Thus the chemisorption results, in concert with the X-ray and TEM measurements, indicate that the starting catalysts are highly dispersed with essentially all the metal atoms in the form of surface atoms.

TABLE 1

Comparison of Hydrogen and Carbon Monoxide Chemisorption on Platinum and Iridium Reforming Catalysts

Catalyst[a]	Adsorbate/metal ratios[b]		
	H(total)/M[c]	H(irrev)/M[d]	CO(irrev)/M[d]
0.3% Pt–Al_2O_3	0.98	0.64	0.78
0.3% Ir–Al_2O_3	2.56	2.04	1.78

[a] Catalysts were reduced at 773 K for 2 hr under hydrogen (500 cm^3/min) at 101 kPa (760 Torr) total pressure.

[b] M = total metal concentration.

[c] Total hydrogen uptake at 0 Torr pressure.

[d] Quantities of hydrogen and carbon monoxide retained at 0 and 100 Torr pressure, respectively, following a 0.17-hr evacuation (10^{-5} Torr) at 298 K.

The acidities of the starting catalysts were estimated by *n*-butylamine adsorption measurements. At a given chloride concentration, the acidities (400–500 μmole/g) of the platinum and iridium on alumina catalysts were indistinguishable (*27*).

B. Cyclohexane Dehydrogenation

The dehydrogenation of cyclohexane to benzene is primarily a metals-catalyzed reaction and is favored at elevated temperatures and low hydrogen partial pressures (*28–31*). Reaction conditions used in these studies were chosen to minimize effects due to heat and mass transfer, product inhibition, and secondary reactions (*2* ,*19*, *32*). The rates of cyclohexane dehydrogenation over platinum and iridium are compared in Table 2. Platinum was found to exhibit a

TABLE 2

Cyclohexane Dehydrogenation[a]: The Influence of Metals on Reaction Patterns

Catalyst	Conversion (mole %)	Rates[b] (mole/hr/g) × 10^2	
		R_{dyd}	R_{hc}
0.3% Pt–Al_2O_3	6.00	80.4	—
0.3% Ir–Al_2O_3	1.60	21.4	0.112

[a] Conditions: 573 K, 101 kPa, WHW = 1130, H_2/cyclohexane = 2.3, 0.6% Cl, 2.0 hr on feed.

[b] R_{dyd} = rate of dehydrogenation; R_{hc} = rate of hydrocracking.

fourfold higher dehydrogenation rate than iridium. Since both catalysts are essentially completely dispersed, the higher activity demonstrated by platinum would persist if comparison was made on a unit surface area basis (*33*). The dehydrogenation rate observed for platinum is in reasonable agreement with reported values (*34, 35*).

Under the relatively mild reaction conditions employed, benzene formation was highly selective over the platinum catalyst. No hydrocracking of the cyclohexane ring was detected. The iridium catalyst, in contrast, displayed a 0.5% selectivity (R_{hc}/R_{dyd}) toward hydrocracked products. Under the more severe reaction conditions employed in reforming (e.g., 770 K, 1000–3000 kPa) the relative quantity of hydrocracked products from an iridium catalyst might be expected to increase. Because of its higher dehydrogenation and lower hydrocracking activities, platinum is a more efficient cyclohexane aromatization catalyst than iridium.

C. *Methylcyclopentane Aromatization*

The conversion of methylcyclopentane to benzene requires the use of a bifunctional catalyst (*36, 37*). Such catalysts simultaneously promote ring expansion (acid function) and dehydrogenation (metal function) reactions. Aromatization is thought to be initiated by the generation of methylcyclopentene on a metal site which is subsequently isomerized to cyclohexene on an acidic alumina site. Concentrations of the isomeric methylcyclopentene and cyclohexene intermediates are low and are governed by equilibria (*38*). Ultimately, by a series of steps, cyclohexene is dehydrogenated to benzene on a metal site. Benzene formation is essentially irreversible at the high temperatures employed in reforming. Under the temperatures and pressures normally used in reforming, the acid-catalyzed ring expansion of methylcyclopentene to cyclohexene is rate controlling. Methylcyclopentane as well as the intermediate methylcyclopentenes can also hydrocrack yielding a mixture of hexanes and lighter gas products. The initial ring opening and secondary hydrocracking reactions are primarily catalyzed by metal sites (*39*). Acid-catalyzed ring opening can, however, become significant if the metal and acid functions are improperly balanced (e.g., the acidity is too high) (*40*). The initial composition of the isomeric hexanes is further modified by subsequent isomerization, cracking, and dehydrocyclization reactions. Thus, optimum benzene yields are to be expected only when the metal and acid chemistries of bifunctional catalysts are judiciously balanced (*41, 42*).

The conversion of methylcyclopentane over platinum and iridium catalysts at 723 K and 1380 kPa total pressure is summarized in Fig. 2. Prior to placement on feed, the catalysts were sulfided *in situ* to breakthrough. Support acidities were maintained as similar as possible by utilizing the same start-of-run chloride concentrations. The platinum catalyst exhibited stable conversion and benzene selectivity levels throughout the 30-hr run. After about 2 hr on feed the conversion level of the iridium catalyst increased fourfold. Accompanying this sharp increase in conversion was a 40% decrease in benzene selectivity and a corresponding large increase in hydrocracking. The onset of high hydrocracking activity is likely associated with sulfur removal from the iridium crystallites. During the first several hours on feed, sufficient sulfur is

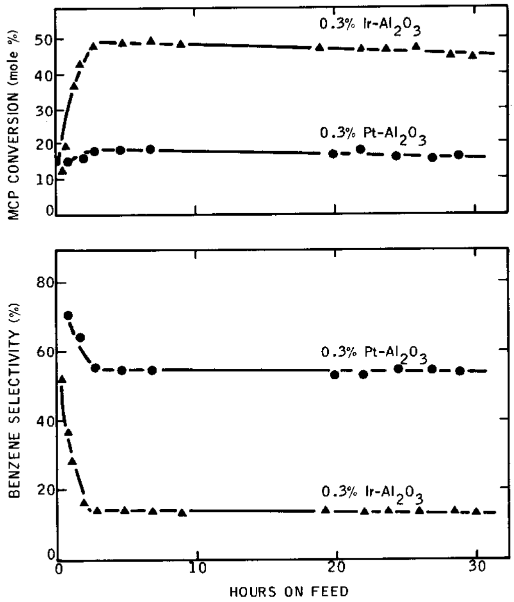

FIG. 2. Methylcyclopentane aromatization: Influence of metals on reaction patterns. Run conditions: 723 K, 1380 kPa, WHW = 40, H_2/MCP = 5, 0.9% Cl(SOR), 1.0 ppm sulfur added to feed.

present from the presulfiding step to moderate the hydrocracking activity of iridium. With time, the sulfur layer is stripped from the catalyst and the high hydrogenolysis activity of iridium dominates the overall conversion pattern (*43*, *44*). Thus, over the 30-hr run a feed sulfur concentration of 1.0 ppm was not high enough to suppress the hydrocracking activity of the iridium catalyst.

The rates of conversion of methylcyclopentane over the platinum and iridium catalysts compared in Fig. 2 are summarized in Table 3. After 24 hr on feed, the lined-out iridium catalyst demonstrated a 3-fold higher conversion level than platinum. Although lower in overall activity, the platinum catalyst exhibited a 1.3-fold higher aromatization rate than iridium. The higher conversion level of the iridium catalyst, compared to platinum, is reflected in a 6-fold higher hydrocracking rate. Initial ring-opening rates, yielding isohexane products, over both platinum and iridium are substantially higher than the rates of formation of lighter hydrocarbons ($C_5^{\ominus}$ products). Within the total $C_6^{\ominus}$ crackate iridium displayed a 5-fold higher fraction of $C_5^{\ominus}$ products than platinum. This behavior is consistent with the higher hydrogenolysis activity of iridium.

Both catalysts exhibited similar end-of-run chloride concentrations. This indicates that the support acidities and, thereby, the acid cracking activities of the catalysts were comparable throughout each run. The iridium catalyst produced a significantly lower coke make than the platinum catalyst. The lower coke make demonstrated by the former catalyst is consistent with the relatively higher hydrocracking activity of iridium. High hydrogenolysis activity should facilitate the removal of carbonaceous residues from metals (*45*). X-Ray diffraction measurements on the recovered catalysts indicated the absence of platinum

TABLE 3

Methylcyclopentane Aromatization[a]: The Influence of Metals on Reaction Patterns

Catalyst	Conversion (mole%)	Rates[b] (mole/hr/g) × 10^2			Weight (%)[c]	
		$C_5^{\ominus}$	i-C_6	Benzene	C	Cl
0.3% Pt–Al_2O_3	16.1	0.049	3.08	4.54	0.47	0.72
0.3% Ir–Al_2O_3	47.0	1.36	17.5	3.47	0.17	0.67

[a] Conditions: 723 K, 1380 kPa, WHW = 40, H_2/MCP = 5, 0.9% Cl(SOR), 1.0 ppm sulfur, 24 hr on feed.

[b] $C_5^{\ominus}$ = rate of conversion of MCP to $C_5^{\ominus}$ products; i-C_6 = rate of conversion of MCP to isohexanes; benzene = rate of conversion of MCP to benzene.

[c] Catalyst inspections, 30 hr on feed.

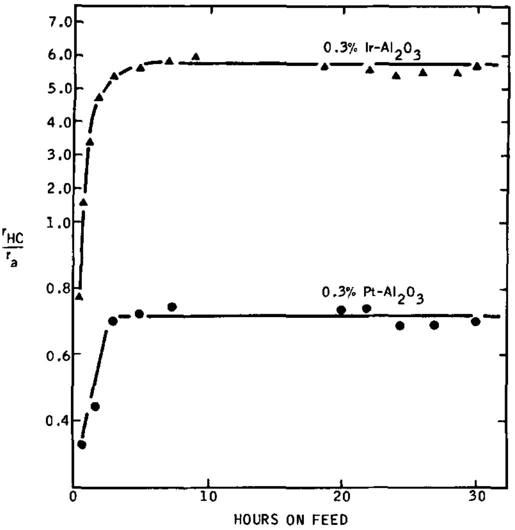

FIG. 3. Methylcyclopentane aromatization: Influence of metals on selectivity patterns. Run conditions: 723 K, 1380 kPa, WHW = 40, H_2/MCP = 5, 0.9% Cl(SOR), 1.0 ppm sulfur added to feed.

and iridium sintering during the on oil cycle.

Catalyst selectivities, as a function of time on feed, are compared in Fig. 3. The r_{HC}/r_a ordinate values represent the ratios of the hydrocracking ($C_5^{\ominus}$ and isohexanes) and aromatization (benzene) rates. Low values for this ratio signify a desirable selectivity pattern. Through the 2- to 30-hr reaction period the r_{HC}/r_a ratios displayed by iridium were eight times larger than those demonstrated by platinum. The relatively high r_{HC}/r_a ratios shown by iridium result primarily from high hydrocracking rates and not low rates of aromatization.

Sulfur added in the form of H_2S or an organic sulfur compound such as thiophene is generally effective in lowering the hydrocracking activity of metals (*8*, *46*, *47*). The basis for the inhibition of hydrocracking caused by sulfur addition is, however, not well understood (*48*). As described above, a feed sulfur concentration of 1.0 ppm could not control the hydrocracking activity of iridium. To better quantify the moderating effects of sulfur, a range of feed sulfur concentrations 0.1 to 10 ppm was investigated. The results of these studies are presented in Table 4. Immediately prior to placement on feed the catalysts were sulfided to breakthrough at 748 K using a dilute H_2S/H_2 mixture. Conversion data were collected after 3 hr on feed to minimize sulfur stripping from the catalyst surface. A 100-fold change in feed sulfur concentration did not markedly alter the

TABLE 4

Methylcyclopentane Aromatization[a]: The Effect of Feed Sulfur on Reaction Patterns

Catalyst	Sulfur (ppm)	Conversion (mole%)	Rates[b] (mole/hr/g) × 10²		r_{HC}/r_a[c]	Weight (%)[d]	
			r_{HC}	r_a		C	Cl
0.3% Pt–Al_2O_3	0.1	20.3	2.91	6.76	0.43	0.30	0.60
	0.5	16.8	2.09	6.00	0.35	0.41	0.57
	1.0	18.0	2.30	6.36	0.36	0.46	0.58
	10.0	20.2	3.32	6.36	0.52	0.49	0.59
0.3% Ir–Al_2O_3	0.1	59.2	23.2	4.77	4.86	0. 0	0.51
	0.5	63.2	24.7	4.67	5.29	0.23	0.51
	1.0	64.6	21.9	4.92	4.45	0.21	0.51
	10.0	46.3	16.6	5.08	3.27	0.28	0.53

[a] Conditions: 748 K, 1380 kPa, WHW = 40, H_2/MCP = 5, 0.6% Cl(SOR), 3.0 hr on feed.

[b] r_{HC} = rate of conversion of MCP to ($C_5^{\ominus}$ + i-C_6) products; r_a = rate of conversion of MCP to benzene.

[c] Ratio of hydrocracking and aromatization rates.

[d] Catalyst inspections, 3 hr on feed.

aromatization rates of either catalyst. Hydrocracking rates exhibited by iridium were observed to decrease by about 30% upon increasing the feed sulfur concentration from 0.1 to 10 ppm. The hydrocracking rates displayed by platinum were, in contrast, found to be relatively insensitive to changes in feed sulfur concentrations. This insensitivity suggests that a steady-state sulfur concentration is readily maintained on platinum. Selectivity patterns, as indicated by the relatively high r_{HC}/r_a ratios, exhibited by iridium were inferior to those shown by platinum throughout the sulfur range investigated. Thus, at normal reforming sulfur concentrations (0.1 to 1.0 ppm), the somewhat higher rates of aromatization and significantly lower r_{HC}/r_a ratios displayed by platinum, when compared to iridium, indicate that platinum is the better catalyst for the aromatization of alkylcyclopentanes.

Coke makes over both catalysts systematically increased with increasing feed sulfur concentrations. This trend is consistent with the ability of sulfur to suppress the hydrocracking activity of metals. At a particular feed sulfur concentration, the coke make demonstrated by iridium was lower than that shown by platinum.

The most significant effects of temperature on the conversion of methylcyclopentane are summarized in Table 5. Rate data are presented after 0.5- and 24-hr reaction periods. The 24-hr data are included in an attempt to clarify the roles sulfur stripping and catalyst deactivation play during the first few hours on feed. Initial (0.5 hr on feed) methylcyclopentane conversions and aromatization rates increased, as expected, with increasing reaction temperature (*31*). In contrast to the 0.5-hr data, catalyst selectivities (r_{HC}/r_a) after 24 hr on feed generally improved with temperature. At temperatures above 773 K, however, both catalysts rapidly deactivated (compare conversions at 0.5 and 24 hr). Deactivation is most likely associated with the enhanced coking rates observed at higher reaction temperatures.

The effect of pressure on the conversion of methylcyclopentane is presented in Table 6. Total conversions were generally observed to be lower at 690 than at 1380 kPa total reaction pressure. The significantly decreased conversion exhibited by iridium

TABLE 5

Methylcyclopentane Aromatization[a]: The Effect of Temperature on Reaction Patterns

Catalyst	T (K)	Conversion (mole%)		$r_a \times 10^2$ [b]		r_{HC}/r_a [c]		Weight (%)[d]	
		0.5 hr	24 hr	0.5 hr	24 hr	0.5 hr	24 hr	C	Cl
0.3% Pt–Al_2O_3	723	14.3	16.1	5.12	4.54	0.33	0.69	0.47	0.72
	748	26.0	16.7	9.13	6.07	0.35	0.31	0.44	0.66
	773	40.1	17.1	15.2	8.77	0.26	0.52	0.80	0.66
	798	54.7	17.9	20.8	2.93	0.25	1.44	2.96	0.60
0.3% Ir–Al_2O_3	723	12.1	47.0	3.25	3.47	0.76	5.45	0.17	0.67
	748	23.1	48.8	6.09	5.26	0.81	3.40	0.21	0.64
	773	33.0	42.4	8.38	7.65	0.87	1.59	0.80	0.54
	798	76.1	37.7	15.0	6.36	1.41	1.48	1.38	0.56

[a] Conditions: 1380 kPa, WHW = 40, H_2/MCP = 5, 0.9% Cl(SOR), 1.0 ppm sulfur.

[b] r_a = rate of conversion of MCP to benzene (mole/hr/g).

[c] Ratio of hydrocracking ($C_5^{\ominus}$ + i-C_6) and aromatization rates.

[d] Catalyst inspections, 30 hr on feed.

TABLE 6

Methylcyclopentane Aromatization[a]: The Effect of Pressure on Reaction Patterns

Catalyst	Pressure (kPa)	Conversion (mole%)	Rates[b] (mole/hr/g) × 10^2			r_{HC}/r_a[c]	Coke[d] (wt%)
			$C_5^{\ominus}$	i-C_6	Benzene		
0.3% Pt–Al_2O_3	690	15.3	0.034	1.37	5.84	0.24	0.90
	1380	16.7	0.066	1.78	6.07	0.31	0.44
0.3% Ir–Al_2O_3	690	19.2	0.61	4.24	4.26	1.14	0.66
	1380	48.8	2.19	15.7	5.26	3.40	0.21

[a] Conditions: 748 K, WHW = 40, H_2/MCP = 5, 0.9% Cl(SOR), 1.0 ppm sulfur, 24 hr on feed.

[b] $C_5^{\ominus}$ = rate of conversion of MCP to $C_5^{\ominus}$ products; i-C_6 = rate of conversion of MCP to isohexanes; benzene = rate of conversion of MCP to benzene.

[c] Ratio of hydrocracking ($C_5^{\ominus}$ + i-C_6) and aromatization rates.

[d] Catalyst inspections, 30 hr on feed.

at 690 kPa results primarily from a lowered hydrocracking rate. Both catalysts displayed slightly lower aromatization rates at 690 than at 1380 kPa. Since enhanced aromatization rates are expected at lower hydrogen partial pressures the lower rates of benzene formation observed must reflect the consequences of catalyst deactivation. Deactivation may be associated with enhanced coke makes, since coke precursors are less readily hydrocracked from the catalyst surface at lower hydrogen pressures. The higher coke makes found on the catalysts operated at lower reaction pressures support this suggestion.

D. *n-Heptane Dehydrocyclization*

The dehydrocyclizaton of paraffins with six or more carbon atoms is generally considered to be a metals-catalyzed reaction (*49–53*). The primary dependency of paraffin dehydrocyclizaton upon metals activity suggests the possibility of different catalyst specificities. When subjected to typical reforming temperatures and pressures, *n*-heptane is converted into a complex mixture of products. For comparative purposes the reaction products have been divided into three groups, namely, a C_1 to C_6 crackate, isoheptanes, and aromatics. Methane through hexane products are formed via cracking reactions on either metal or acid sites. Methane and ethane are generated on metal sites while propane and isobutane are the products of acid site cracking (*54, 55*). The preferential formation of propane and isobutane on acid sites is accounted for by considering the stabilities of intermediate carbonium ions (*56*). Although isomerization can occur on metal sites, the isoheptanes are most likely generated by a dual-functional mechanism (*57*). The dual-function mechanism proceeds by the initial dehydrogenation of *n*-heptane to 1-heptene on a metal site. The 1-heptene intermediate is subsequently adsorbed on an acid site where it undergoes skeletal isomerization to a mixture of isoheptenes. The initial composition of the isoheptenes is near that predicted by equilibrium considerations (*58*). In a final step the isoheptenes are hydrogenated on a metal site. Toluene is thought to be generated by an initial dehydrogenation, producing 1-heptene, followed by ring closure. Both dehydrogenation and ring closure are catalyzed by metal sites (*59, 60*). Ring closure on platinum is generally accepted to occur by the direct formation of a six-carbon atom ring (*61*). Following ring closure the methylcyclohexane intermediate is rapidly dehydrogenated to toluene on a metal site. Minor quantities of benzene are produced by a combination of toluene dealkylation and hexane dehy-

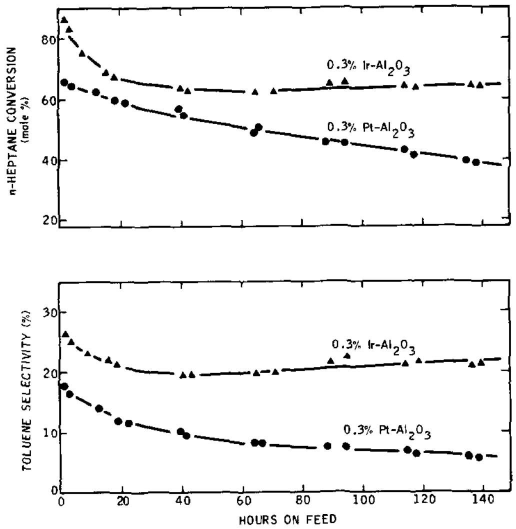

FIG. 4. *n*-Heptane dehydrocyclization: Influence of metals on reaction patterns. Run conditions: 768 K, 1380 kPa, WHW = 21.1, $H_2/n\text{-}C_7 = 5$, 0.6% Cl(SOR), no sulfur added to feed.

drocyclization. Trace amounts of xylenes are likely generated by toluene disproportionation (*62*). From the above description it is apparent that the conversion of *n*-heptane is complex and thus, potentially highly catalyst dependent. Ultimate toluene yields are predicated upon the ability of metals to catalyze ring closure and subsequent dehydrogenation reactions. Toluene yields will also be influenced by catalyst acidity, which if too high, will produce excessive amounts of cracked products (*12*).

n-Heptane conversion patterns over platinum and iridium are contrasted in Fig. 4. The experiments summarized in Fig. 4 were carried out in the absence of added feed sulfur and the catalyst were not subjected to a presulfiding step. After an initial activity decrease during the first 20 hr on feed, the iridium catalyst displayed an essentially constant conversion level throughout the remaining 140-hr run. Conversion over platinum, in contrast, steadily declined over the entire test period. In addition to its higher activity, iridium also demonstrated a twofold higher toluene selectivity than platinum.

The rates of conversion of *n*-heptane over platinum and iridium are summarized in Table 7. In the absence of added feed

TABLE 7

n-Heptane Dehydrocyclization[a]: The Effect of Feed Sulfur on Reaction Patterns

Catalyst	Sulfur (ppm)	Conversion (mole%)	Rates[b] (mole/hr/g) × 10^2			r_c/r_d[c]	Weight (%)[d]	
			$C_4^{\ominus}$	i-C_7	Toluene		C	Cl
0.3% Pt–Al_2O_3	0	38.8	0.80	5.58	0.55	1.45	0.86	0.21
	0.1	42.8	0.91	6.24	0.64	1.42	1.84	0.29
	0.5	39.3	0.84	5.82	0.48	1.75	1.12	0.14
	1.0	38.7	0.94	5.53	0.45	2.09	2.02	0.30
	5.0	34.2	1.08	4.91	0.39	2.76	1.54	0.17
	10.0	37.8	0.99	5.40	0.44	2.25	1.22	0.27
0.3% Ir–Al_2O_3	0	66.0	3.14	4.72	3.14	1.00	0.50	0.24
	0.1	50.4	1.73	5.07	1.94	0.89	1.18	0.22
	0.5	46.7	1.58	4.43	2.21	0.72	0.86	0.22
	1.0	49.2	1.64	5.02	2.03	0.81	0.91	0.21
	5.0	52.5	1.72	5.44	2.20	0.78	0.96	0.19
	10.0	54.4	1.64	5.78	2.42	0.68	0.48	0.21

[a] Conditions: 768 K, 1380 kPa, WHW = 21.1, H_2/n-heptane = 5, 0.6% Cl(SOR), 135 hr on feed.

[b] $C_4^{\ominus}$ = rate of conversion of *n*-heptane to $C_4^{\ominus}$ gas products; i-C_7 = rate of conversion of *n*-heptane to isoheptanes; toluene = rate of conversion of *n*-heptane to toluene.

[c] Ratio of hydrocracking ($C_4^{\ominus}$) and dehydrocyclization (toluene) rates.

[d] Catalyst inspections, 140 hr on feed.

sulfur, iridium demonstrated a dehydrocyclization rate six times higher than that of platinum. The dehydrocyclization rate exhibited by the platinum catalyst is in good agreement with literature values reported for platinum on alumina catalysts (*6*, *8*, *63*, *64*). The rates of cracking ($C_4^{\ominus}$ formation) over these two catalysts increased in the same direction found for dehydrocyclization. Isomerization rates (i-C_7 formation) were observed to be inversely proportional to the dehydrocyclization rates. The apparent inverse relationship indicates that iridium dehydrocyclizes isoheptanes more efficiently than platinum. Catalyst selectivities, in the absence of added feed sulfur, as a function of time on feed are contrasted in Fig. 5. The r_c/r_d ordinate values are the ratios of the hydrocracking ($C_4^{\ominus}$) and dehydrocyclization (toluene) rates. Low values for this ratio signify a desirable selectivity pattern. Platinum demonstrated a steadily increasing selectivity ratio with time on feed. Although both the hydrocracking and dehydrocyclization rates decreased throughout the run, the increasing r_c/r_d ratios displayed by platinum result from a relatively more rapid decline in dehydrocyclization activity. The r_d/r_d ratios shown by iridium were, in contrast, found to increase only slowly with time. Since increasing r_c/r_d ratios are indicative of catalyst deactivation, the activity maintenance of iridium on a paraffinic feedstock is better than that of platinum. End-of-run chloride concentrations were found to be essentially the same for both catalysts. The significantly different reaction rates exhibited by platinum and iridium must, therefore, reflect different metal specificities since contribution to the rates from acid centers would be expected to be comparable. In support of this conclusion, experiments carried out with different start-of-run chloride concentrations (0.6 to 1.5%) showed that the individual conversion rates increased with chloride concentration. Overall catalyst selectivities, however, were essentially insensitive to changes in support acidity (chloride concentration).

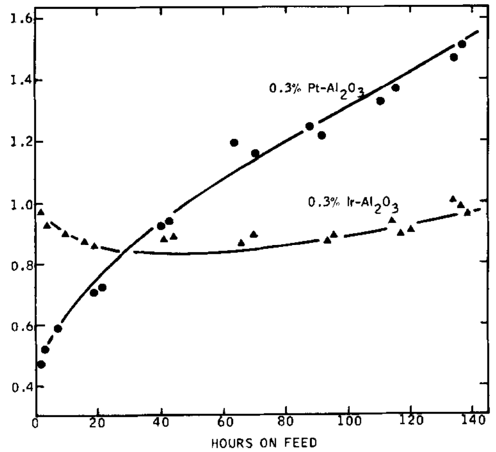

FIG. 5. *n*-Heptane dehydrocyclization: Influence of metals on selectivity patterns. Run conditions: 768 K, 1380 kPa, WHW = 21.1, $H_2/n\text{-}C_7 = 5$, 0.6% Cl(SOR), no sulfur added to feed.

The effects of sulfur on the conversion rates of *n*-heptane are also summarized in Table 7. Prior to introduction of feed the catalysts were sulfided *in situ* to breakthrough using a dilute H_2S/H_2 mixture. After 135 hr on feed the extent of *n*-heptane conversion was found to be essentially insensitive to a 100-fold change in feed sulfur concentration. A 20% decrease in *n*-heptane conversion, however, occurred when the iridium catalyst was presulfided and subsequently placed on a sulfur-containing feed. The conversion level exhibited by platinum was, in contrast, not measurably changed by the presence of parts per million sulfur concentrations. Both the hydrocracking and dehydrocyclization rates of the iridium catalyst were significantly decreased upon presulfiding and utilizing a 0.1-ppm sulfur-containing feed. Higher feed sulfur concentrations, however, did not further decrease these rates. The hydrocracking rates of a presulfided platinum catalyst were found to increase slightly with increasing feed sulfur concentrations. The dehydrocyclization rates demonstrated by platinum were, in contrast, not strongly altered by changes in sulfur concentrations.

Selectivities, as measured by the r_c/r_d ratios, of the iridium catalyst improved with increasing concentrations of feed sulfur. The decreasing r_c/r_d ratios observed for iridium indicate that sulfur suppresses hydrocracking to a greater extent than dehydrocyclization. In contrast, the selectivity of platinum decreased with increasing sulfur concentration. On the basis then of its higher dehydrocyclization activity and superior selectivity, iridium is a better paraffin aromatization catalyst than platinum with or without sulfur in the feed.

End-of-run chloride concentrations were found to be essentially insensitive to feed sulfur concentrations. Although the data are somewhat scattered, coke makes were generally observed to be higher in the presence of sulfur-containing feedstocks. The enhanced coke make on sulfided catalysts is consistent with the ability of sulfur to decrease the hydrocracking activity of metals, which in turn, lowers the rate of removal of carbonaceous deposits (*65*).

The effects of temperature on the rates of conversion of *n*-heptane are summarized in Table 8. Prior to collection of rate data, the catalysts were lined out for 40 hr at 768 K and 1380 kPa total pressure. Low conversions were maintained so as to minimize mass and heat transfer limitations. The rate values reported for each temperature are the average of at least two measurements. No catalyst deactivation occurred during data collecton since conversion profiles determined in a descending temperature sequence were reproduced in a subsequent ascending temperature sequence. Under the differential conversion conditions employed considerable quantities of saturated cyclo-C_7 products, namely, 1,2-dimethylcyclopentane, 1,3-dimethylcyclopentane, ethylcyclopentane, and methylcyclohexane were detected in the reaction products. Under normal reforming conditions the concentrations of these toluene precursors are negligibly small. Conversion of these toluene precursors was found to increase with temperature as noted by the increasing toluene/cyclo-C_7 ratios with reaction temperature. At 768 K the relative toluene formation rates of iridium and platinum were

TABLE 8

n-Heptane Dehydrocyclization[a]: The Effect of Temperature on Reaction Patterns

Catalyst	*T* (K)	Conversion (mole%)	Rates[b] (mole/hr/g) × 10^2				$\frac{\text{Toluene}^c}{\text{Cyclo-}C_7}$	$\frac{r_c^d}{\text{Cyclo-}C_7}$
			$C_4^{\ominus}$	i-C_7	Toluene	Cyclo-C_7		
0.3% Pt–Al_2O_3	718	1.19	0.75	1.83	0.013	0.66	0.02	1.14
	733	2.09	1.19	3.66	0.043	0.79	0.05	1.51
	748	3.79	2.09	7.05	0.15	1.24	0.12	1.69
	768	7.05	4.19	12.1	0.57	2.31	0.25	1.81
	783	10.5	7.47	15.6	1.21	3.61	0.34	2.07
0.3% Ir–Al_2O_3	718	1.86	1.24	2.18	0.34	1.28	0.27	0.97
	733	3.21	2.09	4.10	0.72	1.98	0.36	1.06
	748	5.00	3.53	6.16	1.33	2.97	0.45	1.19
	768	9.36	6.97	10.5	2.75	5.34	0.52	1.31
	783	13.2	10.9	13.3	3.80	7.13	0.53	1.53

[a] Conditions: 1380 kPa, WHW = 274, H_2/*n*-heptane = 5, 0.9% Cl(SOR), 0.5 ppm sulfur, data collected between 40 and 50 hr on feed.

[b] $C_4^{\ominus}$ = rate of conversion of *n*-heptane to $C_4^{\ominus}$ gas products; i-C_7 = rate of conversion of *n*-heptane to isoheptanes; toluene = rate of conversion of *n*-heptane to toluene; cyclo-C_7 = rate of conversion of *n*-heptane to all C_7 cyclization products.

[c] Ratio of toluene and cyclo-C_7 rates.

[d] Ratio of hydrocracking $C_4^{\ominus}$ and cyclo-C_7 rates.

found to be 4.8 and 1.0, respectively. These relative rates compare well with those reported above using integral conversion data. Throughout the temperature range investigated iridium exhibited a more desirable selectivity than platinum (compare r_c/cyclo-C_7 ratios). Thus the dehydrocyclization rates and selectivity patterns exhibited by platinum and iridium under differential reaction conditions closely parallel those shown at much higher conversion levels.

The effects of pressure on the initial conversion rates of *n*-heptane at two different reaction temperatures are summarized in Table 9. As expected, the rates of dehydrocyclization at a given temperature over platinum and iridium were found to be higher at 690 than at 1380 kPa total pressure. For a given reaction temperature, platinum exhibited a higher pressure sensitivity (compare r_d (690)/r_d (1380) ratios) for toluene formation than did iridium. The disparate hydrogen pressure dependencies suggest that the mechanism of dehydrocyclization may be different over these two metals. The pressure sensitivity for toluene formation was noted to decrease with increasing temperature. This trend indicates that the rate-determining step may also change with temperature. The rate of formation of olefinic intermediates may not be, for example, rate limiting at higher reaction temperatures. Hydrocracking rates at 748 K were observed to decrease, as expected, at lower hydrogen partial pressures. At 698 K, however, the hydrocracking rates displayed by platinum were found to be higher at 690 than at 1380 kPa total pressure. This seemingly contradictory behavior can be rationalized if it is assumed that a proportionally higher fraction of olefins are hydrocracked under the lower temperature and pressure condition. This assumption is reasonable since olefins hydrocrack more readily than paraffins and their formation is favored at lower pressures (*66*). The rates of formation of isoheptanes were found to be relatively insensitive to changes in reaction pressure. Since isomerization likely proceeds through an olefin intermediate, the absence of a strong pressure dependency indicates that skeletal isomerization rather than paraffin dehydrogenation is rate controlling under the reacton conditions employed (*58*).

TABLE 9

n-Heptane Dehydrocyclization[a]: The Effect of Pressure on Reaction Patterns

Catalyst	T (K)	Pressure (kPa)	Conversion (mole%)	Initial rates[b] (mole/hr/g) × 10^2			$r_d(690)^c / r_d(1380)$
				$C_4^{\ominus}$	i-C_7	Toluene	
0.3% Pt–Al_2O_3	698	690	27.9	0.21	4.91	0.51	3.2
		1380	23.0	0.10	4.41	0.16	
	748	690	58.8	0.78	7.44	3.04	1.3
		1380	60.7	1.09	8.07	2.31	
0.3% Ir–Al_2O_3	698	690	25.2	0.48	3.89	0.52	1.4
		1380	26.7	0.57	4.17	0.38	
	748	690	53.7	1.87	4.53	4.14	1.0
		1380	78.0	3.92	5.21	3.99	

[a] Conditions: WHW = 21.1, H_2/*n*-heptane = 5, 0.9% Cl(SOR), 1.0 ppm sulfur, 1.5 to 3.5 hr on feed.

[b] $C_4^{\ominus}$ = rate of conversion of *n*-heptane to $C_4^{\ominus}$ gas products; i-C_7 = rate of conversion of *n*-heptane to isoheptanes; toluene = rate of conversion of *n*-heptane to toluene.

[c] Ratio of dehydrocyclization rates at 690 and 1380 kPa, respectively.

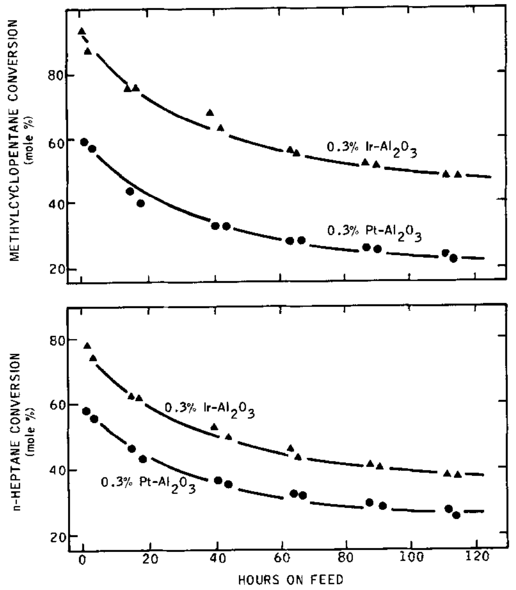

FIG. 6. Competitive conversion of methylcyclopentane and n-heptane: Influence of metals on reaction patterns. Run conditions: 768 K, 1380 kPa, WHW = 22.2, 0.9% Cl(SOR), feed: methylcyclopentane (34.4 mole%), n-heptane (53.3 mole%), i-xylenes (12.3 mole%), 0.5 ppm sulfur, H_2/feed = 5.

E. Competitive Conversion of Methylcyclopentane and n-Heptane

The influence of catalyst on the conversion of a synthetic mixture of methylcyclopentane (34.4 mole%), n-heptane (53.3 mole%), and isomeric xylenes (12.3 mole%) is shown in Fig. 6. Under the reaction conditions employed less than 0.5 mole% of the starting xylenes was cracked to light gas products. The stability of the aromatic ring is in agreement with the observations of Rohrer and Sinfelt (*67*). Thus, the participation of xylene in the overall conversion of the mixture can be neglected. Over a 115-hr reaction period the initial conversion levels of methylcyclopentane and n-heptane decreased by about 50%. For both catalysts the relative conversion ratio, methylcyclopentane/n-heptane, corrected to an equal molar basis, remained constant throughout the course of the experiment. Corrected methylcyclopentane/n-heptane conversion ratios were calculated to be 1.4 and 2.0 for platinum and iridium, respectively. These ratios indicate that 1.4 and 2.0 methylcyclopentane molecules react for each n-heptane molecule converted. The preferential conversion of methylcyclopentane is consistent with the relative ease of naphthene aromatization compared to paraffin dehydrocyclization. The higher methylcyclopentane/n-heptane conversion ratio displayed by iridium results from a higher methylcyclopentane hydrocracking rate.

The rates of benzene and toluene production, as a function of time, are shown in Fig. 7. Throughout the run length, the aromatization of methylcyclopentane was higher over platinum than iridium, while iridium demonstrated a consistently higher n-heptane dehydrocyclization rate than platinum. These relative activity orders are identical to those obtained with pure feedstocks. Rate data, collected after 112 hr on feed, are summarized in Table 10. Lined-out methylcyclopentane aromatization rates were found to be 1.3 times higher over platinum than iridium. n-Heptane dehydro-

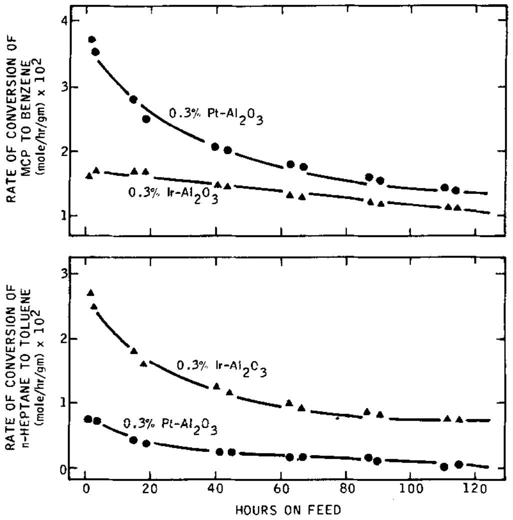

FIG. 7. Competitive conversion of methylcyclopentane and n-heptane: Influence of metals on reaction rates. Run conditions: 768 K, 1380 kPa, WHW = 22.2, 0.9% Cl(SOR), feed: methylcyclopentane (34.4 mole%), n-heptane (53.3 mole%), i-xylenes (12.3 mole%), 0.5 ppm sulfur, H_2/feed = 5.

TABLE 10

Rates of Conversion of a Synthetic Mixture Composed of Methylcyclopentane, *n*-Heptane, and Isomeric Xylenes[a]

Catalyst	Methylcyclopentane				*n*-Heptane				Weight (%)[b]	
	Conversion (mole%)	Rates (mole/hr/g) × 10^2			Conversion (mole%)	Rates (mole/hr/g) × 10^2			C	Cl
		$C_4^{\ominus}$	i-C_6	Benzene		$C_4^{\ominus}$	i-C_7	Toluene		
0.3% Pt–Al_2O_3	23.7	0.01	0.48	1.43	25.9	0.19	2.49	0.15	1.53	0.16
0.3% Ir–Al_2O_3	47.5	0.27	2.31	1.14	37.1	0.67	2.16	0.74	0.56	0.22

[a] Feed component (mole%): methylcyclopentane (34.4), *n*-heptane (53.3), isoxylenes (12.3). Component flow rates: 0.083 mole methylcyclopentane/hr/g; 0.118 mole *n*-heptane/hr/g; 0.035 mole isoxylenes/hr/g. Run conditions: 768 K, 1380 kPa, WHW = 22.2, 0.9% Cl(SOR), 0.5 ppm sulfur, 112 hr on feed.

[b] Catalyst inspections, 115 hr on feed.

cyclization rates were, in contrast, 5 times higher over iridium than platinum. Thus the relative aromatization and dehydrocyclization rates found for the synthetic mixture are in good agreement with the rate ratios obtained with pure components (see Tables 5 and 7 for comparison). After normalizing (taking into account the relative molar concentration of methylcyclopentane), the aromatization rates displayed by platinum and iridium are 20 to 40% lower for the mixture than with pure methylcyclopentane. Similarly, the normalized *n*-heptane dehydrocyclization rates for the mixture were found to be 35 to 50% lower than those obtained using neat *n*-heptane. Thus paraffin dehydrocyclization appears to be somewhat more strongly suppressed in the mixture than naphthene aromatization. The decreased rates of benzene and toluene formation found for the mixture indicate that competitive adsorption–desorption processes may be retarding these transformations. The adsorption of aromatic molecules on both metal and acid sites is known to slow down various hydrocarbon conversion processes (*68–70*). The presence of xylene in the reaction mixture may therefore hinder the adsorption and subsequent conversion of both methylcyclopentane and *n*-heptane to aromatics.

After 112 hr on feed, the normalized benzene/toluene formation rate ratios were calculated to be 14.9 and 2.4, respectively, for platinum and iridium. The significant disparity in these ratios further indicates that platinum is a more efficient naphthene aromatization catalyst than iridium. Conversely it can be stated that iridium is a more efficient paraffin dehydrocyclization catalyst than platinum.

As was found with pure feedstock runs, the methylcyclopentane component of the mixture was more extensively hydrocracked over iridium than platinum. Overall selectivity patterns, however, were not appreciably changed by the presence of paraffinic and aromatic hydrocarbons. What is observed for the mixture is a slowing down of each pathway open to the methylcyclopentane molecule. For the *n*-heptane component, the relative dehydrocyclization rates and selectivity patterns are similar to those established for pure *n*-heptane. As observed for methylcyclopentane, added naphthene and aromatic hydrocarbons suppress the rates of each reaction path exhibited by *n*-heptane. Thus, the rate-moderating effects observed for the synthetic mixture are similar to those encountered with complex naphtha feedstocks.

4. SUMMARY

The above model compound reforming studies have shown that individual hydrocarbon conversion rates and product selectivities are markedly dependent upon the metal component of a bifunctional reforming catalyst. The most significant differences demonstrated by platinum and iridium catalysts can be summarized as follows: Under typical reforming conditions the rates and selectivities for benzene formation from cyclohexane and methylcyclopentane are higher over platinum than iridium. The lower benzene selectivity exhibited by iridium results from hydrocracking of the cyclohexane and methylcyclopentane rings. Iridium was, in contrast, found to be a more active and selective *n*-heptane dehydrocyclization catalyst than platinum. Feed sulfur levels of 0.1 to 10 ppm had little effect on the *n*-heptane conversion pattern of platinum, but significantly lowered the hydrocracking activity of iridium. The observed model compound chemistry differences indicated that a combination of metals may provide reforming benefits. Such benefits have in fact been clearly demonstrated for platinum–iridium bimetallic catalyst systems (*13*).

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