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The Effects of Rhenium and Sulfur on the Maintenance of Activity and Selectivity of Platinum/Alumina Hydrocarbon Conversion Catalysts

II. Experiments at Elevated Pressure

V. K. SHUM,[1] J. B. BUTT, AND W. M. H. SACHTLER[2]

Ipatieff Laboratory, Departments of Chemistry and Chemical Engineering, Northwestern University, Evanston, Illinois, 60201

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With *n*-hexane conversion at 770 K, 1.5 MPa and a hydrogen/hydrocarbon molar ratio of 11 as the test reaction, $PtRe/Al_2O_3$ prepared by coimpregnation has been found to differ from a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3. In particular, $PtRe/Al_2O_3$ shows a high selectivity for hydrogenolysis which is characteristic of PtRe alloy formation. Compared with runs at 0.1 MPa, the rate of deactivation and the selectivity for dehydrocyclization are much lower at 1.5 MPa. It is suggested that stepwise dehydrogenation of hexane to hexatriene followed by cyclization may be an important route for dehydrocyclization near atmospheric pressure. The presence of 1 ppm (mol) H_2S in the gaseous feed significantly reduces hydrogenolysis, and also improves the maintenance of both activity and selectivity of $PtRe/Al_2O_3$. The formation of PtRe alloy particles is favored by chlorine in the Al_2O_3 support. The results are consistent with a previously proposed model which assumes that the reorganization of adsorbed hydrocarbonaceous deposits to pseudographitic entities which cannot be volatilized *in situ* is strongly impeded by the protruding S atoms firmly adsorbed on the Re atoms of the PtRe alloy surface. It appears that enhanced activity maintenance can be attributed to changes in the atomic topography of the catalyst metal surface.

I. INTRODUCTION

Bimetallic catalysts for hydrocarbon conversion reactions have received considerable attention in the past 15 years. The addition of a second metallic element such as Re or Sn enhances considerably the activity maintenance of the traditional reforming catalyst, Pt supported on acidic γ-alumina. The Pt–Re combination has gained widespread commercial acceptance. Since the first introduction of $PtRe/Al_2O_3$, the most popular view to explain its characteristic catalytic behavior has been that of alloy formation (see references in Part I (*1*)). But the discussion continues particularly on the specific mechanism of how PtRe alloy formation effects the improved stability characteristics of this catalyst under conditions of industrial reforming.

In Part I, results of catalytic tests done at atmospheric pressure with halide-free catalysts have been reported. These results strongly suggest that PtRe alloy particles dominantly contribute to the overall catalytic action of $PtRe/Al_2O_3$ even though several valence states of Re may exist simultaneously on the working catalyst surface. The combined action of rhenium and sulfur has been shown to be crucial for the superior stability of the working $PtRe/Al_2O_3$ catalyst (*1*). These results are consistent with a model which assumes that the adsorbed S preferentially fixed on the Re atoms of the PtRe alloy surface cannot be easily removed under process conditions, and that these protruding S_{ads} species impede the reorganization of hydrocarbonaceous fragments (which are in quasi-equilibrium with gas phase hydrogen) to pseudographitic en-

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[1] Present address: Amoco Oil Company, Research and Development Department, P.O. Box 400, Naperville, Ill. 60566.

[2] To whom correspondence should be addressed.

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tities (which cannot be volatilized *in situ*) (*2*).

Conversions measured at atmospheric pressure are insufficient to predict the steady state of catalytic processes at 1–3 MPa, typical for industrial operating conditions. Unsaturated compounds, including mono-, di-, and triolefins, adsorbed carbenes, carbynes, and allyl carbenium ions are known to be important reaction intermediates and coke precursors. The concentrations of these unsaturates under steady state conditions depend strongly on the total pressure even at constant hydrogen/hydrocarbon ratio.

A second factor limiting the generalization of our previous results is due to our decision to limit the number of variables by using halide-free alumina supports. The present study at elevated total pressure therefore includes chloride-containing Pt/Al_2O_3 and $PtRe/Al_2O_3$ catalysts. Model reaction studies with sulfur-free and sulfur-containing *n*-hexane and *n*-heptane feeds were conducted at 1.5 MPa total pressure.

Because of the complex network of reactions involved in the reforming of hydrocarbons on bifunctional catalysts, a clarification of the terminology used in this paper is appropriate. "Cracking" is used as a general term which includes metal-catalyzed, acid-catalyzed, and bifunctionally catalyzed C—C bond fission. "Hydrogenolysis" refers to metal-catalyzed cracking. "Hydrocracking" refers to bifunctionally catalyzed cracking. Acid-catalyzed cracking is simply referred to as "acid cracking." "Dehydrocyclization" refers to the formation of an aromatic hydrocarbon and hydrogen from an alkane. "Cyclization" refers to the formation of a five-membered ring cycloalkane and hydrogen from an alkane.

II. EXPERIMENTAL

Materials. Nonchlorided $PtRe/Al_2O_3$ catalysts were prepared by incipient wetness coimpregnation of the γ-Al_2O_3 support (Cyanamid PHF) with aqueous solutions of $Pt(NH_3)_4(NO_3)_2$ and NH_4ReO_4. Nonchlorided Pt/Al_2O_3 catalysts were prepared similarly with $Pt(NH_3)_4(NO_3)_2$ as the precursor. Details of preparation of these nonchlorided catalysts have been previously reported (*1*, *3*). The nonchlorided catalysts used comprised 0.3% wt Pt/Al_2O_3 and 0.3% wt Pt–0.3% wt Re/Al_2O_3.

Two industrial reforming catalysts which contain significant levels of chloride were also used. They included Pt/Al_2O_3 (Cyanamid SN-6003, 1/16-in. extrudate; 0.3% wt Pt, 0.9% wt Cl) and $PtRe/Al_2O_3$ (Cyanamid SN-6004, 1/16-in. extrudate; 0.3% wt Pt, 0.3% wt Re, 0.9% wt Cl). The alumina support in these two technological catalysts is of Cyanamid PHF grade as in the nonchlorided catalysts.

The liquid hydrocarbon reagents used included *n*-hexane (Aldrich 13938-6 and Baker 9304) and *n*-heptane (Aldrich 15487-3), both of about 99% purity as determined by GLC. They were used without further purification unless stated otherwise. Hydrogen and helium were of ultrahigh purity grade from Matheson and Linde, respectively. The gases were further purified by passing them through 4A molecular sieve filters (Linde) to remove moisture. Where applicable, the carbon disulfide used was of AR grade from Mallinckrodt.

Apparatus and procedure. The catalysts were tested for the conversion of hydrocarbons in hydrogen under continuous-flow in a microcomputer-controlled fixed-bed reactor which follows the design of Snel (*4*). Residual sulfur which remained on the wall of the SS316 reactor after experiments with sulfur-containing feeds was removed by purging continuously in hydrogen flow at 770 K for 1 week. Following such treatment, catalysts loaded into the reactor showed behavior identical to catalysts in a reactor which had previously not been used with sulfur-containing feeds. Reaction products were analyzed by on-line GLC using a Hewlett–Packard 5890A gas chromatograph (FID, subambient temperature programming) with a 50-m crosslinked methyl silicone fused silica capillary column (Hewlett-Packard 19091S-001). Peak areas were determined using a Hewlett-Packard 3392A integrator. Details of the experimental setup are reported in (*3*). The procedure for data evaluation was the same as in (*5*).

Prior to reaction, catalysts were dried in flowing He at 770 K for 1 h and then reduced in flowing H_2 at 770 K for 2 h *in situ* in the reactor all at 0.4 MPa pressure. The following conditions were used for the reaction: 770 K, 1.5 MPa, and 11 mol/mol H_2/hydrocarbon. In experiments with sulfur-containing feeds, the liquid hydrocarbon was mixed with 6 ppm(mol) carbon disulfide. The carbon disulfide should be converted to hydrogen sulfide under the reducing conditions in the gas phase contacting the catalyst at reaction temperature. The mole fraction of hydrogen sulfide in the gaseous reaction mixture was thus 1 ppm in these experiments.

III. RESULTS

1. Active Sites on PtRe/Al_2O_3 Catalysts

It was shown in Part I (*1*) that a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 catalysts showed catalytic properties markedly different from a cosupported PtRe/Al_2O_3 catalyst prepared by coimpregnation for *n*-hexane conversion at 770 K and 0.1 MPa. In particular, the cosupported PtRe catalyst showed a high selectivity for hydrogenolysis which is characteristic of Pt–Re alloy formation. It was concluded that PtRe alloy particles are dominantly responsible for the catalytic performance of PtRe/Al_2O_3 under the conditions used. This does not exclude that other rhenium species may coexist with the PtRe alloy on the working catalyst surface.

The following two intimate physical mixtures of catalysts were compared for *n*-hexane conversion at 770 K and 1.5 MPa:

(a) 250 mg 0.3% wt Pt/Al_2O_3 + 250 mg 0.3% wt Re/Al_2O_3 (short notation: Pt + Re)

(b) 250 mg 0.3% wt Pt– 0.3% wt Re/Al_2O_3 + 250 mg γ-Al_2O_3 (short notation: PtRe)

The support particles in these mixtures were of 60–80 mesh (0.18–0.25 mm). These physical mixtures were prepared by mechanically shaking the component catalysts together in a vial. The platinum, rhenium and alumina contents were identical in both mixture systems. Total conversion and selectivity data are presented in Table 1. The selectivity patterns of the two catalyst systems show distinct differences. The cosupported PtRe catalyst displays a higher selectivity for cracking than the physically mixed Pt + Re catalyst. Conversely, the selectivity for isomerization and cyclization is higher for the Pt + Re catalyst. These

TABLE 1

n-Hexane Conversion[a] on Pt + Re and PtRe Catalysts

Catalyst[c]	Time (h)	Conv. (%)	Selectivity[b] (%)				
			S_{cr}	S_{is+cy}	S_{dhc}	M	C_1/C_3
Pt + Re	2	38	23	72	5	8	1
	10	28	21	74	5	8	1
PtRe	2	41	45	53	2	4	3
	10	30	33	65	2	6	2

[a] Reaction conditions: 770 K, 1.5 MPa, 11 mol/mol H_2/HC; WHSV(Pt + Re) = 11; WHSV(PtRe) = 17.

[b] Abbreviations: cr, cracking; is + cy, isomerization and cyclization; dhc, dehydrocyclization.

[c] See text.

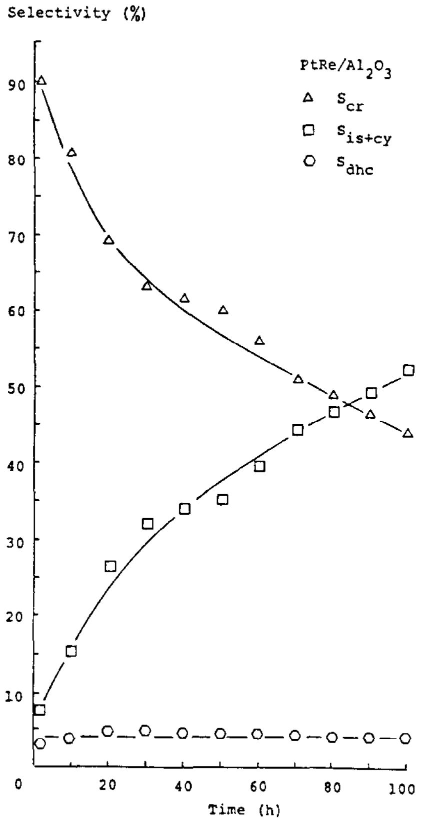

FIG. 1. Selectivity vs time-on-stream for the PtRe/Al_2O_3 catalyzing the conversion of sulfur-free *n*-hexane. Reaction conditions: $T = 770$ K, $P = 1.5$ MPa, $H_2/HC = 11$, WHSV = 11.

differences in performance between the PtRe and Pt + Re catalysts are qualitatively the same as those observed at 0.1 MPa total pressure.

Also included in Table 1 are values of the molar ratio of methane to propane, C_1/C_3, in the product gas and the fission parameter, *M*. Methane is produced only on metal sites whereas propane can be formed either on metal or acid sites. The fission parameter as defined in (*5*) is given by

$$M = \frac{1}{C_1} \sum_{i=2}^{5} \sum_{j} (6 - i)\, C_{i,j}$$

where $C_{i,j}$ is the molar concentration of the isomer *j* of the hydrocarbon with *i* carbon atoms in the molecule. Summation is made first over all isomers with given *i*, then over all values of *i*. C_1 is the molar concentration of methane. Both *M* and C_1/C_3 are used to characterize the way of chain fission. When $M \simeq 1$, specific terminal fission prevails; when $M > 1$, fission is random or even preferentially concentrated toward bonds in the middle of the molecule; when $M < 1$, multiple fission (hydrogenolytic degradation to C_1 fragments) predominates. The results for the fission parameter and the C_1/C_3 ratio show that the cosupported PtRe catalyst displays less fission toward internal bonds thus leading to a more significant level of methane than the physically mixed Pt + Re catalyst. These results show that the chemical interaction of Pt with Re in the cosupported catalyst prevails in its catalytic action at both 0.1 and 1.5 MPa of operating pressure; and they eliminate the possibility that more or

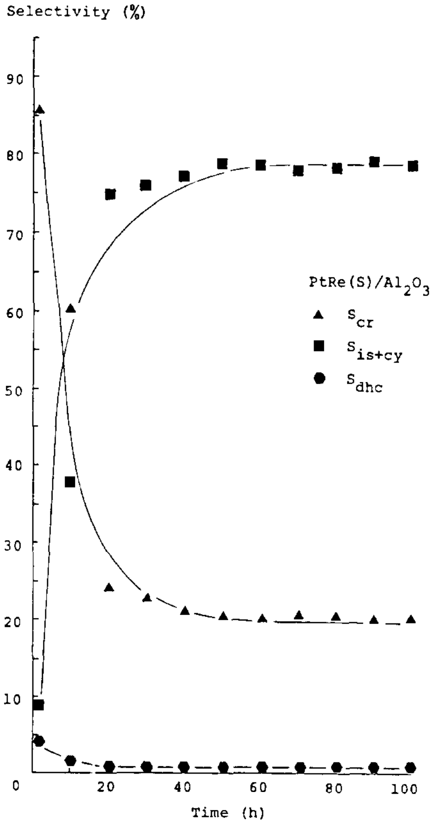

FIG. 2. Selectivity vs time-on-stream for PtRe/Al_2O_3 catalyzing the conversion of sulfur-containing *n*-hexane. Reaction conditions: $T = 770$ K, $P = 1.5$ MPa, $H_2/HC = 11$, $y(CS_2) = 0.5$ ppm, WHSV = 11.

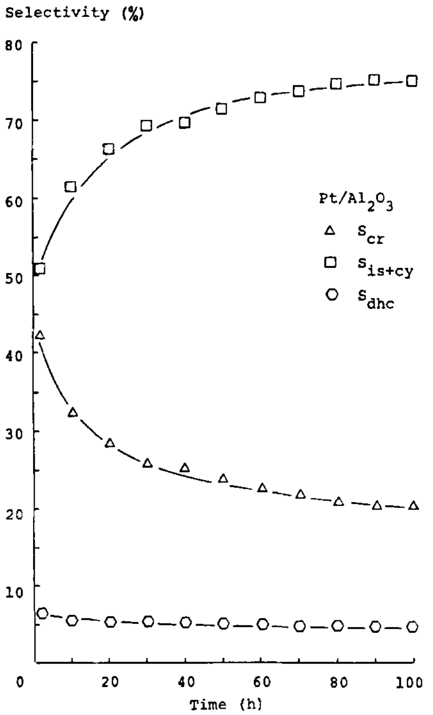

FIG. 3. Selectivity vs time-on-stream for Pt/Al_2O_3 catalyzing the conversion of sulfur-free *n*-hexane. Reaction conditions: see Fig. 1.

stronger sites in the cosupported sample are the cause of the increased selectivity for cracking. The results do not, however, exclude that some interparticle migration of Re or Pt might also have taken place in the physical mixture, as was previously shown by Bolivar *et al.* (*6*) for low surface area supports. If such migration takes place, it is, however, insufficient to achieve the same degree of interaction between Re and Pt as in the cosupported sample.

2. *Effects of Sulfur on Activity and Selectivity*

a. Halide-free catalysts. In Fig. 1 the selectivity vs time data for *n*-hexane conversion on $PtRe/Al_2O_3$ under sulfur-free conditions are shown. During short time-on-stream when the catalyst is presumably relatively free of coke, $PtRe/Al_2O_3$ shows a cracking selectivity of ~90%. As time-on-stream increases, the selectivity for cracking decreases while that for isomerization and cyclization increases steadily. The selectivity for dehydrocyclization remains very low and practically unchanged throughout the 100 h run. In Fig. 2, the selectivity vs time data are shown for *n*-hexane conversion on $PtRe/Al_2O_3$ with 1 ppm (mol) of H_2S in the gaseous feed. Note the much faster changes in selectivity and that a steady state level is reached. The changes in selectivity during the first 10–20 h represent the titration of the metal sites by adsorbed sulfur; simultaneously some sulfidation of the reactor wall will take place. After 10 h, about 4×10^{18} molecules of H_2S had entered the reactor which contained about 5×10^{18} Re atoms in the catalyst bed.[3] Adsorbed sulfur drastically reduces the selectivity for cracking resulting in a compensating increase in the selectivity for isomerization and cyclization. The selectivity for the dehydrocyclization of *n*-hexane to benzene is reduced by sulfur.

The selectivity vs time data of Pt/Al_2O_3 for the conversion of sulfur-free and sulfur-

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[3] When comparing these results with those obtained in other laboratories or under industrial conditions, it should be remembered that the steady-state coverage of a metal with sulfur depends on a number of parameters, including the sulfur content of the feed, its hydrogen content and the temperature. If the steady state is approximated by thermodynamic equilibrium of

$$H_2S + M \rightleftharpoons M\text{-}S_{ads} + H_2$$

where M is an adsorption site consisting of an ensemble of metal atoms, it follows that the standard free energy of this equilibrium is given by

$$\Delta G^\circ = RT \ln[H_2S]/[H_2] = RT \ln r.$$

In the present work, complete conversion of the CS_2 added to the liquid feed corresponds to $r = 10^{-6}$. For industrial reactors where the sulfur is present as an impurity of the feed, r can be calculated as follows:

$$r = wM/sR$$

where w = weight fraction of sulfur in the hydrocarbon feed
M = average molecular weight of the hydrocarbon feed
s = atomic weight of sulfur
R = H_2/hydrocarbon molar ratio.

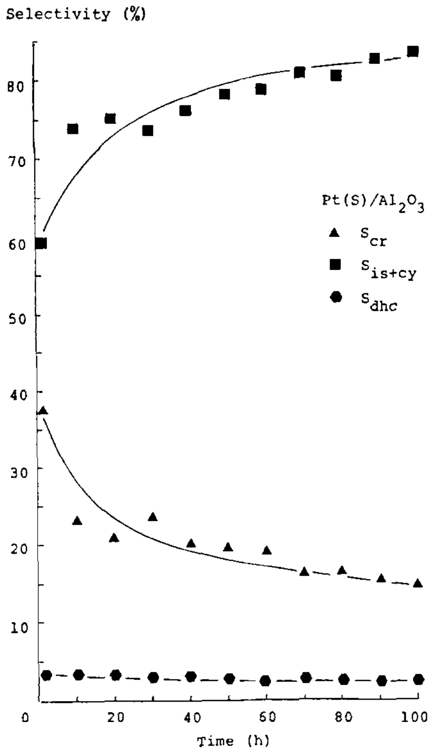

FIG. 4. Selectivity vs time-on-stream for Pt/Al$_2$O$_3$ catalyzing the conversion of sulfur-containing *n*-hexane. Reaction conditions: see Fig. 2.

containing *n*-hexane are shown in Figs. 3 and 4. When compared with PtRe/Al$_2$O$_3$, the monometallic sample displays a relatively high selectivity for isomerization and cyclization which increases with time. Correspondingly, the selectivity for cracking is lower and decreases with time. The selectivity for dehydrocyclization is very low and decreases slightly with time. The changes in selectivity brought about by sulfidation of Pt/Al$_2$O$_3$ are all in the same direction as those caused by sulfiding PtRe/Al$_2$O$_3$, albeit smaller in magnitude. In contrast to PtRe/Al$_2$O$_3$, no constant selectivity levels are established for Pt/Al$_2$O$_3$ exposed to the sulfur-containing feed. Remarkable differences in catalyst deactivation are revealed by the conversion data in Fig. 5. Both PtRe/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ deactivate steadily in a sulfur-free feed, and both show sharp drops in initial activity due to sulfur. However, after this period of sulfidation PtRe/Al$_2$O$_3$ displays an excellent activity maintenance, whereas Pt/Al$_2$O$_3$ continues to lose activity during the 100 h of operation.

b. Chloride-containing catalysts. In Fig. 6, the selectivity vs time data for *n*-hexane conversion on PtRe/Al$_2$O$_3$-Cl under sulfur-free conditions are shown. As with Cl-free PtRe/Al$_2$O$_3$, PtRe/Al$_2$O$_3$-Cl shows an extraordinarily high selectivity for cracking, and this selectivity decreases with time-on-stream albeit more slowly than that of PtRe/Al$_2$O$_3$. Correspondingly, the selectivity for isomerization and cyclization increases gradually with time-on-stream. PtRe/Al$_2$O$_3$-Cl shows a selectivity for dehydrocycliza-

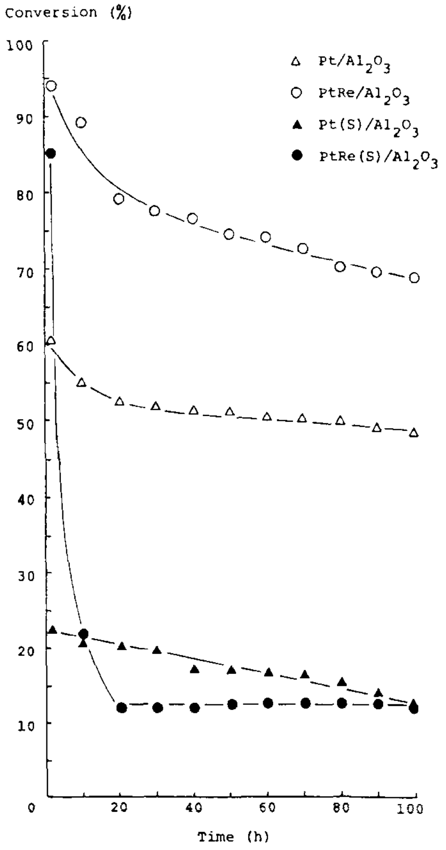

FIG. 5. Total conversion vs time-on-stream for Pt/Al$_2$O$_3$ and PtRe/Al$_2$O$_3$ catalyzing the conversion of sulfur-free and sulfur-containing *n*-hexane. Reaction conditions: see Figs. 1–4.

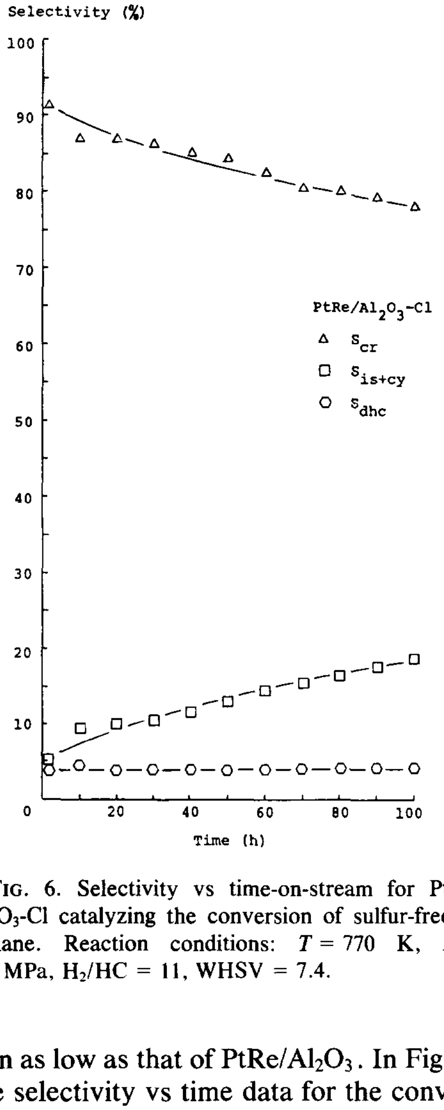

FIG. 6. Selectivity vs time-on-stream for PtRe/Al$_2$O$_3$-Cl catalyzing the conversion of sulfur-free *n*-hexane. Reaction conditions: $T = 770$ K, $P = 1.5$ MPa, H$_2$/HC = 11, WHSV = 7.4.

tion as low as that of PtRe/Al$_2$O$_3$. In Fig. 7, the selectivity vs time data for the conversion of sulfur-containing *n*-hexane on PtRe/Al$_2$O$_3$-Cl are shown. As with Cl-free PtRe/Al$_2$O$_3$, sulfidation of PtRe/Al$_2$O$_3$-Cl reduces drastically the selectivity for cracking resulting in a concomitant increase in the selectivity for isomerization and cyclization. The selectivity for the dehydrocyclization of n-hexane is reduced by sulfidation. PtRe/Al$_2$O$_3$-Cl like its Cl-free counterpart displays an excellent selectivity maintenance for the conversion of a sulfur-containing feed. We should mention that the experiments using sulfur-containing feeds were carried out with the Cl-free catalyst first. Purging the reactor with pure hydrogen at reaction temperature to remove residual sulfur was not done in between runs with sulfur-containing feeds. Compared with the Cl-free catalyst, the sharper initial changes caused by sulfiding the Cl-loaded catalyst might be due to the possibility that in the latter case the catalyst experienced a feed somewhat richer in H$_2$S, as the reactor wall had already been conditioned with sulfur.

The selectivity vs time data of Pt/Al$_2$O$_3$-Cl for the conversion of sulfur-free and sulfur-containing n-hexane are shown in Figs. 8 and 9. These results are very similar to those obtained for Cl-free Pt/Al$_2$O$_3$. Chloride does not seem to affect the product distribution in any significant way under the conditions used. This is surprising as sulfur

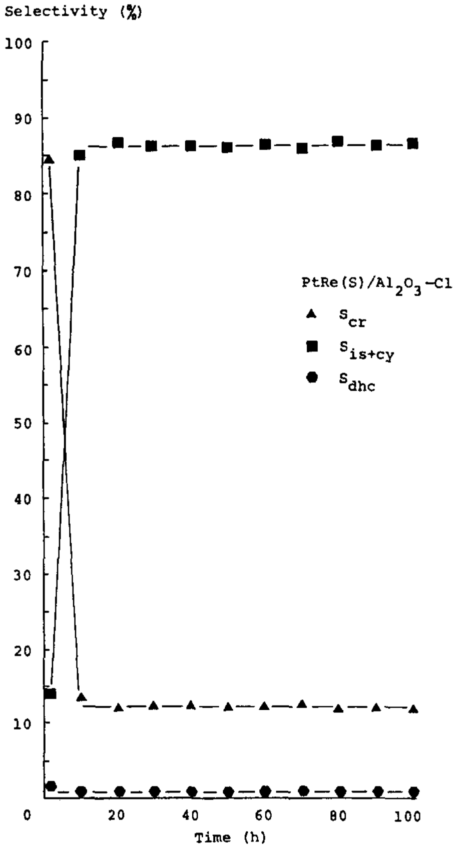

FIG. 7. Selectivity vs time-on-stream for PtRe/Al$_2$O$_3$-Cl catalyzing the conversion of sulfur-containing *n*-hexane. Reaction conditions: $T = 770$ K, $P = 1.5$ MPa, H$_2$/HC = 11, y(CS$_2$) = 0.5 ppm, WHSV = 7.4.

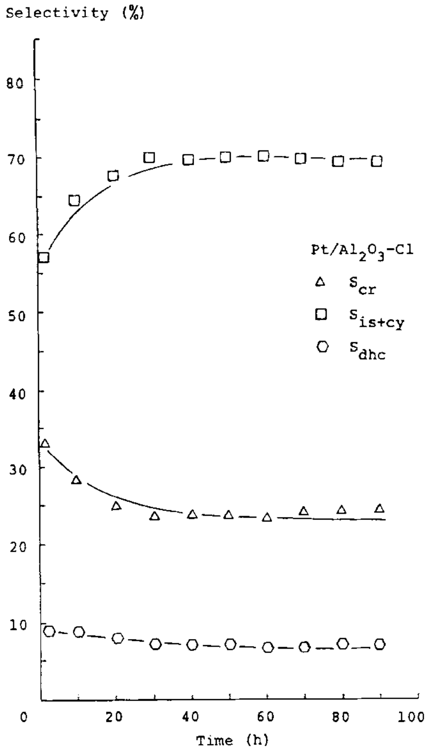

FIG. 8. Selectivity vs time-on-stream for Pt/Al_2O_3-Cl catalyzing the conversion of sulfur-free *n*-hexane. Reaction conditions: see Fig. 6.

will reduce cracking by metal sites; the remaining cracking due to acid sites might have been expected to be stronger for Al_2O_3-Cl.

The total conversion vs time data for Cl-loaded $PtRe/Al_2O_3$ and Pt/Al_2O_3 catalysts in the absence and presence of sulfur are summarized in Fig. 10. The behavior of these Cl-loaded catalysts is qualitatively the same as that of Cl-free catalysts described above; again the sulfided platinum–rhenium catalyst displays an excellent maintenance of activity.

Chemical analyses were carried out to determine how much chloride, if any, may have been stripped from the catalyst after activation and reaction with *n*-hexane for 100 h under the conditions used. The analysis was done by leaching the chloride from the catalyst with deionized water at room temperature overnight followed by titrating the resultant solution with silver nitrate. The chloride content of a fresh catalyst determined as such agrees to within ±10% with the manufacturer's data. After about 100 h of reaction, a catalyst which contains 0.9% wt Cl when fresh has been found to contain typically ~0.6% wt Cl.

n-Heptane conversion on $PtRe/Al_2O_3$-Cl was also investigated both with and without carbon disulfide present in the feed. Total conversion and selectivity results are shown in Fig. 11. Selectivity results are shown in Figs. 12 and 13. As with *n*-hexane, the PtRe catalyst shows very good maintenance of activity and selectivity upon sulfidation. Sulfidation reduces the selectivity for cracking, it increases the selectivity for isomerization and cyclization, and it has no significant effect on the selectivity for the dehydrocyclization of *n*-heptane to toluene under the conditions used.

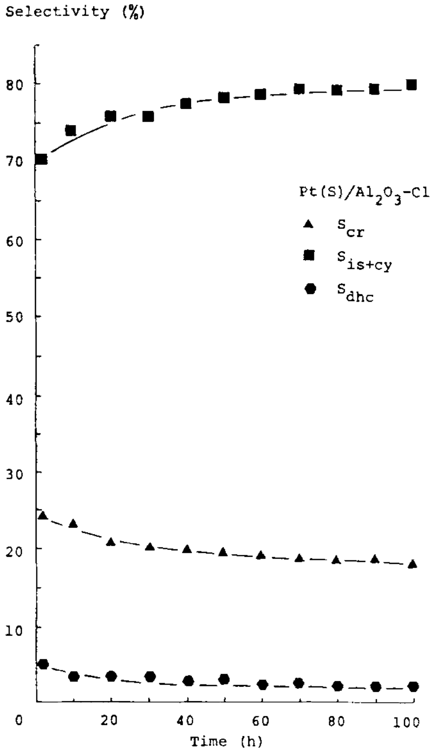

FIG. 9. Selectivity vs time-on-stream for Pt/Al_2O_3-Cl catalyzing the conversion of sulfur-containing *n*-hexane. Reaction conditions: see Fig. 7.

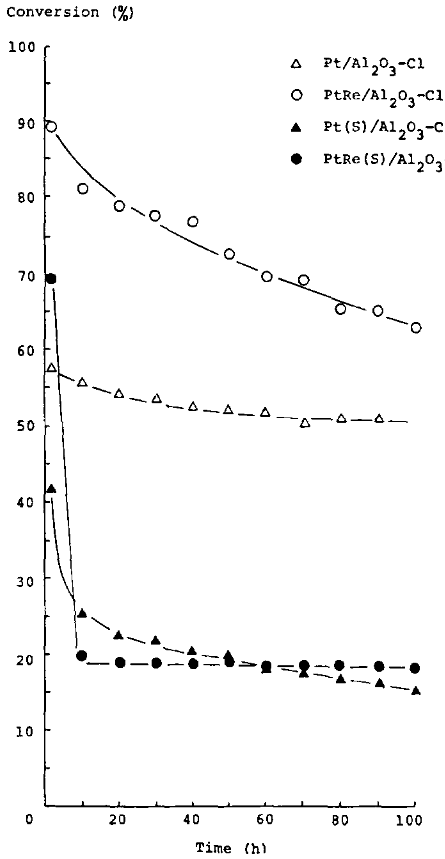

FIG. 10. Total conversion vs time-on-stream for Pt/Al_2O_3-Cl and PtRe/Al_2O_3-Cl catalyzing the conversion of sulfur-free and sulfur-containing n-hexane. Reaction conditions: see Figs. 6–9.

3. *Chain Fission Characteristics and Balance of Activities between Metal and Acid Functions*

The fission parameter, M and the molar ratio of methane to propane, C_1/C_3 may be used as measuring sticks for the chain fission characteristics of a catalyst. In addition, the ratio C_1/C_3 may be used as an approximate relation to describe the balance of activities between metal and acid in a bifunctional catalyst. Cracking of n-paraffins on acid sites produces mainly C_3 and C_4 fragments because of carbenium ion chemistry (7). Methane is produced on metal sites only. The fission parameters and the methane to propane ratios of various cata-

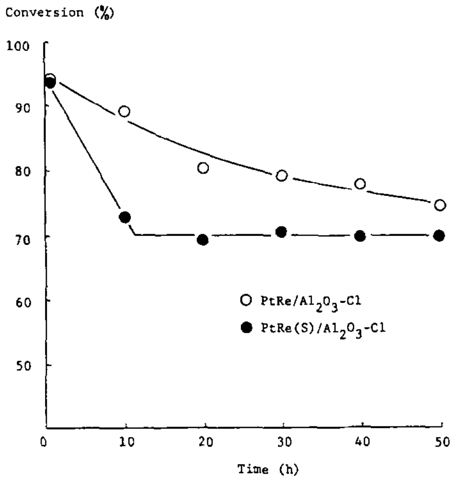

FIG. 11. Total conversion vs time-on-stream for PtRe/Al_2O_3-Cl catalyzing the conversion of sulfur-free and sulfur-containing n-heptane. Reaction conditions: $T = 770$ K, $P = 1.5$ MPa, $H_2/HC = 11$, $y(CS_2) = 0.5$ ppm, WHSV = 7.7.

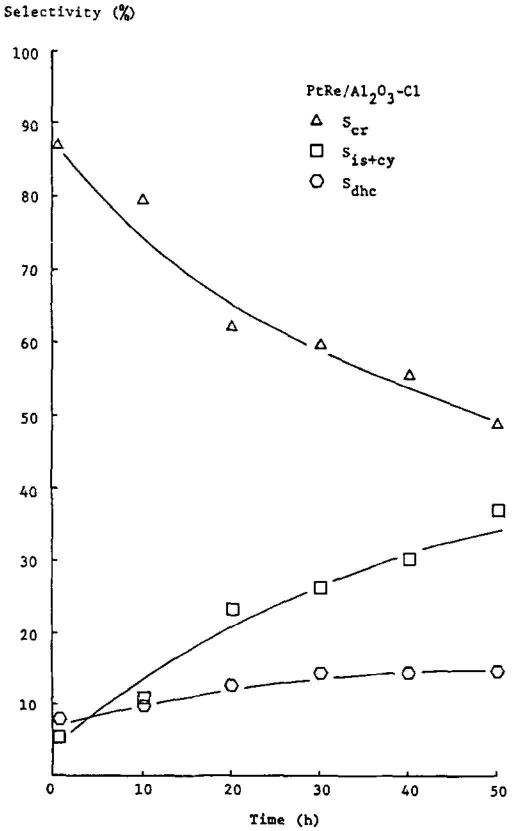

FIG. 12. Selectivity vs time-on-stream for PtRe/Al_2O_3-Cl catalyzing the conversion of sulfur-free n-heptane. Reaction conditions: see Fig. 11.

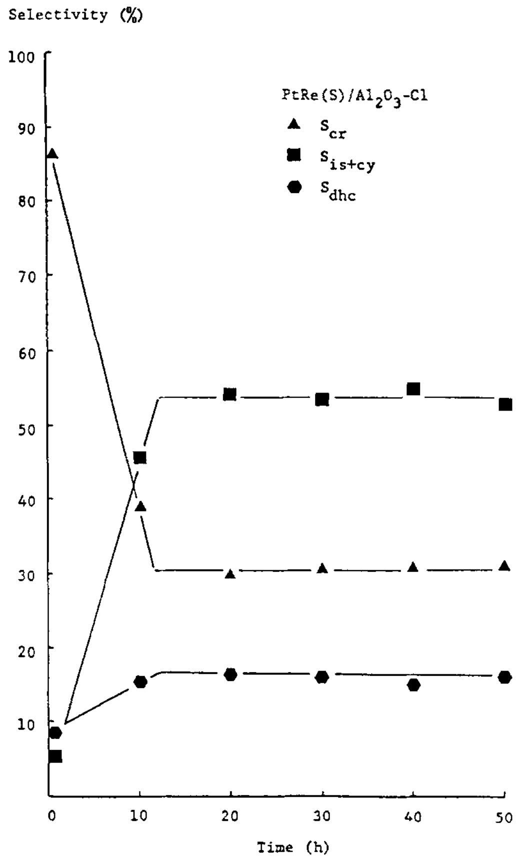

FIG. 13. Selectivity vs time-on-stream for $PtRe/Al_2O_3$-Cl catalyzing the conversion of sulfur-containing *n*-heptane. Reaction conditions: see Fig. 11.

lysts described above for *n*-hexane conversion are summarized in Tables 2 and 3, respectively.

On both unsulfided $PtRe/Al_2O_3$ and unsulfided $PtRe/Al_2O_3$-Cl, C_1/C_3 decreases and M increases with time-on-stream. For short time-on-stream, both catalysts characteristically display multiple fission ($M < 1$) producing large amounts of methane more so with $PtRe/Al_2O_3$-Cl. As these catalysts deactivate, random fission or fission towards middle bonds becomes more significant. The contributions by the metal function to catalysis is significant on these catalysts, this is particularly true on fresh catalysts according to the C_1/C_3 ratios.

TABLE 2

Fission Parameter, *M*

Catalyst	Time (h)		
	2	50	90
PtRe	0.9	5	5
PtRe(S)	—	16	16
PtRe-Cl	0.5	2	3
PtRe(S)-Cl	—	17	17
Pt	7	9	10
Pt(S)	—	13	13
Pt-Cl	8	10	10
Pt(S)-Cl	—	14	14

Sulfidation drastically reduces multiple fission such that both $PtRe(S)/Al_2O_3$ and $PtRe(S)/Al_2O_3$-Cl at steady state show essentially the same low C_1/C_3 ratios and high M values characteristic of internal C—C bond fission. This confirms that sulfidation and coking affect the metal function predominantly. The *M* parameters also reveal that the large differences in fission characteristics between Pt and PtRe all but vanish upon sulfidation.

IV. DISCUSSION

The experimental results comparing cosupported $PtRe/Al_2O_3$ with an intimate physical mixture of separately supported Pt/Al_2O_3 and Re/Al_2O_3 show that these two catalyst systems have distinctly different catalytic properties. In particular, cosupported $PtRe/Al_2O_3$ exhibits a high selectiv-

TABLE 3

Ratio of Methane to Propane, C_1/C_3

Catalyst	Time (h)		
	2	50	90
PtRe	11	2	2
PtRe(S)	—	0.4	0.4
PtRe-Cl	32	6	4
PtRe(S)-Cl	—	0.4	0.4
Pt	1	1	0.9
Pt(S)	—	0.5	0.5
Pt-Cl	1	0.9	0.9
Pt(S)-Cl	—	0.5	0.5

ity for cracking. Also, the two catalyst systems show quite different cracking patterns with methane being the dominant product on the cosupported PtRe catalyst. The differences in performance between these catalyst systems at 1.5 MPa are qualitatively the same as those observed at 0.1 MPa. The high cracking activity of the cosupported PtRe/Al_2O_3 catalyst observed over this wide range of operating pressures is characteristic of Pt–Re alloy formation. Biloen *et al.* (8) showed that both unsupported Pt_4Re alloy powder and silica-supported PtRe alloy particles are very selective for hydrogenolysis. Betizeau *et al.* (9) and Haining *et al.* (10) found that a maximum in hydrogenolysis activity exists as a series of alumina-supported Pt–Re catalysts is traversed, and that catalytic activity is not a linear combination of the platinum and rhenium contents. The present results indicate that PtRe alloy particles dominantly contribute to the catalytic action of working PtRe/Al_2O_3 not just at atmospheric pressure but also at the elevated pressure typically used in industrial reforming.

The changes in selectivity caused by sulfidation at 1.5 MPa are in the same direction as those observed at atmospheric pressure on the same catalysts (*1*) and silica-supported catalysts (*8*). These changes in selectivity are rationalized in terms of the ensemble effect of alloy catalysis (*11–13*). Sulfidation with such a dilute stream under the present conditions affects predominantly the metal function (*14–16*), and it has been shown that no bulk sulfide phase is formed under these conditions (*8*). Adsorbed sulfur thus reduces the number of contiguous metal atoms available for the formation of chemisorption complexes. There is general agreement that larger ensembles are required for hydrogenolysis than for metal-catalyzed isomerization and cyclization; (de)hydrogenation can however occur on the smallest ensembles (*12, 13*). Hydrogenolysis is thus significantly reduced by sulfidation. Sulfur bonds much more strongly to rhenium than to platinum (*17*), so sulfur should preferentially cap the surface Re atoms of PtRe alloy particles as indeed shown previously (*8*). It has also been found by temperature-programmed desorption of adsorbed sulfur in hydrogen up to 773 K over presulfided catalysts that Pt/Al_2O_3 retains only about one-sixth of the amount of adsorbed sulfur retained on Re/Al_2O_3 or PtRe/Al_2O_3 (*18*). This sulfur adsorbed on Pt might be expected to exist in a dynamic equilibrium with gas phase hydrogen sulfide and hydrogen. Therefore, the selectivity of sulfided Pt/Al_2O_3 still shows some changes with time-on-stream, whereas that of sulfided PtRe/Al_2O_3 remains constant. Coke deposition on Pt lowers the number of large Pt ensembles; consequently the selectivity for cracking decreases also for sulfided Pt, but its *M* value does not change.

The dramatic changes in selectivity caused by sulfur adsorbed on metal indicate that metal-catalyzed reactions play a significant role in the catalysis of the bifunctional PtRe/Al_2O_3 catalyst with or without chloride. This point is further corroborated by the high C_1/C_3 ratios observed on these catalysts. The high hydrogenolysis activity and high level of multiple fission of unsulfided PtRe alloy particles compared with monometal Pt can be rationalized by assuming that Re—C bonds are stronger than Pt—C bonds so that the rate-limiting step in hydrogenolysis on monometal Pt is the fission of C—C bonds whereas that on monometal Re is the desorption of methane. The observed volcano-shaped curve of hydrogenolysis activity (*10*) as a series of Al_2O_3-supported Pt-Re catalysts is traversed with the maximum in activity at about 60% rhenium is then explained by accepting that the rate of C—C bond fission increases steadily and the rate of desorption of methane falls steadily as the rhenium content of PtRe catalysts increases (*10*). In this way, the multiple fission characteristic of PtRe alloys, particularly the Re-rich alloys (*10*) can also be understood. The strong Re—C bonds lead to a multi-adsorbed species which is inevitably strongly dehydrogenated. Further reactions are mainly confined to places of primary adsorption, i.e., several internal C—C bonds. So multiple fission producing a large amount of methane results. Coke deposition as the catalyst ages reduces multiple fission by reducing the size of metal ensembles and consequently lowering the chance for multiple adsorption.

The results which show that unsulfided $PtRe/Al_2O_3$-Cl exhibits more multiple fission (lower M, higher C_1/C_3) and slower decline in the selectivity for cracking than unsulfided $PtRe/Al_2O_3$ suggest that there is perhaps a higher degree of alloying in the chlorided catalyst. The speculation that chlorination enhances the extent of alloying in a $PtRe/Al_2O_3$ catalyst is not without analogy in another bimetal reforming catalyst. Lieske and Völter (*19*) recently showed that in $PtSn/Al_2O_3$ chlorination enhances the reduction of tin and the extent of Pt—Sn alloying because of the high mobility of chlorided Pt and/or Sn oxycomplexes relative to purely oxidic Pt and/or Sn complexes on the support surface, and this mobility is a necessity for establishing sufficient proximity of Pt and Sn species and consequently for a higher degree of alloy formation. An analogous situation may be found in a $PtRe/Al_2O_3$ catalyst. Note that the redispersion of crystalline Pt during regeneration makes use of the high mobility of a chlorided Pt oxy-complex (*20*).

The major differences in catalytic results of experiments done at 1.5 MPa reported in this paper and those done at 0.1 MPa reported previously (*1*) are that the overall rate of deactivation of an unsulfided catalyst and the selectivity for dehydrocyclization are both considerably lower at 1.5 MPa. At 0.1 MPa, it was observed that presulfidation considerably retards the deactivation due to coke deposition of $PtRe/Al_2O_3$. While initially the activities of sulfided catalysts are lower than those of the corresponding unsulfided catalysts, the activity for sulfided $PtRe/Al_2O_3$ after some time-on-stream is higher than that of the unsulfided, but coke-deactivated catalyst. For Pt/Al_2O_3, the activity of the presulfided catalyst remains below that of the unsulfided sample. The situation is reproduced in Fig. 14 from data reported in Part I (*1*). At 1.5 MPa, no crossing of curves is observed even after 100 h of reaction (see Figs. 5 and 10) because the deactivation rate at elevated pressure is much lower also for unsulfided $PtRe/Al_2O_3$. A rough estimate of the location of the crossing point by means of a deactivation kinetic analysis following the method of Levenspiel (*21*) shows that at 1.5 MPa the conversion on unsulfided $PtRe/Al_2O_3$ would fall to the level of the sulfided catalyst after about 380 h on stream (*3*). The reliability of this extrapolation is about ±20%.

Since the deactivation rate is much lower in the present measurements at 1.5 MPa than in our earlier measurements at 0.1 MPa, it was a point of concern whether the lower deactivation rate may still be ascribed to the formation of carbonaceous overlayers. Low level impurities in the feed might be suspected to cause the slow deactivation observed at elevated pressure. In order to clarify this question, a few runs were carried out with an ultrapure feed which was stored over liquid KNa alloy and

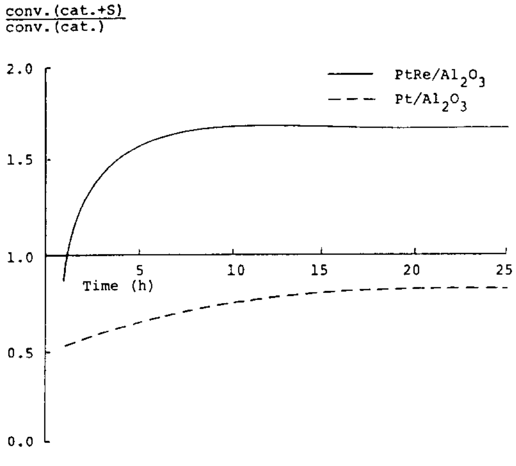

FIG. 14. Ratio of the total conversion exhibited by a presulfided catalyst to that exhibited by an unsulfided catalyst for *n*-hexane conversion. Reaction conditions: T = 773 K, P = 0.1 MPa, H_2/HC = 11.

then distilled off. (We are indebted to C. M. Tsang for carrying out these experiments in the same reactor as used throughout this study.) Higher conversions and lower deactivation rates were indeed observed with this ultrapure feed, but the cracking selectivity decreased with time on stream. As this decrease was mainly due to reduced methane formation, we conclude that it is predominantly the metal function of the bifunctional catalyst system which gets deactivated. In one run where a higher than usual H_2/HC ratio was used, viz. $H_2/HC = 28$ instead of 11, the cracking selectivity decreased from 60 to 40% within 22 h on stream. We therefore feel that it is justified to consider metal deactivation by carbonaceous overlayers as one of the causes of catalyst deactivation and have focused on this aspect in our discussion.

The lowering of the deactivation rate and of the selectivity for dehydrocyclization by raising the total pressure while keeping the temperature and hydrogen/hydrocarbon ratio constant are probably due to a common cause. There is evidence that at low pressure one path of dehydrocyclization is stepwise dehydrogenation followed by cyclization (hexene, hexadiene, hexatriene, cyclohexadiene, benzene) (*22, 23*). Increasing the total pressure 15 times while keeping the temperature and hydrogen/hydrocarbon ratio constant results in drastic reductions in the equilibrium levels of dienes and trienes. Such reductions in the formation of dienes and trienes would necessarily result in a lower dehydrocyclization yield. Extensively dehydrogenated species are also important coke precursors. Reducing the steady state level of unsaturated molecules, therefore, will also reduce coke deactivation. The hexatriene pathway of dehydrocyclization has been proven to occur on Te-NaX at about 770 K and near atmospheric pressure (*24*). Increasing evidence supports the importance of this pathway on Pt catalysts at reforming temperatures and near atmospheric pressure (*25–27*).

The present results show that the chloride content has very little effect on product distributions for *n*-hexane conversion except in the case of PtRe/Al_2O_3 where chloride may enhance alloying, as discussed above. This is quite surprising since experience with industrial naphtha reforming suggests otherwise (*28*). It is conceivable that the 0.3% wt of chloride which is apparently stripped from the catalyst is very important for the acidity of alumina, whereas the ~0.6% wt present after use are less acidic, perhaps located in subsurface positions as reported recently for Pt/Al_2O_3 and PtSn/Al_2O_3 (*29*). This explains why during industrial reforming traces of chloride-containing compounds are continuously added to the naphtha feed to maintain the acidity of the alumina.

The excellent maintenance of activity and selectivity as well as the beneficial changes in selectivity caused by sulfidation of PtRe/Al_2O_3 show that the combined action of rhenium and sulfur is crucial for the superior performance of PtRe/Al_2O_3. The present results are consistent with our model to rationalize the enhanced stability of working PtRe/Al_2O_3 as described in detail previously (*1, 2*), i.e., protruding S_{ads} on Re ensembles in the surface of PtRe particles impede the transformation of hydrocarbonaceous "soft coke" to pseudographitic "hard coke."

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