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Dehydrogenation of cyclohexane on catalysts containing noble metals and their combinations with platinum on alumina support

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Abstract

The dehydrogenation of cyclohexane over catalysts containing 0.35 wt% of each of the following metals: Pt, Rh, Re, U, PtIr, PtRh, PtRe and PtU on γ-Al_2O_3 was carried out in a pulsed micro-reactor system at the temperature range 200–500°C. PtRh catalyst was the most active for the dehydrogenation of cyclohexane in the temperature range 250–350°C. The catalyst containing Rh was the most active for hydrogenolysis of cyclohexane to propane due to the higher percentage of d-bond character of Rh. It was found that the introduction of U inhibits the activity of Pt catalyst for the dehydrogenation. The effect of chlorine and fluorine contents (1, 3 and 6 wt%) on the activities of these catalysts were investigated. Optimum halogen content was found to be 3% for dehydrogenation enhancement which may be attributed to improved hydrogen spillover as well as to increased dispersion of the metal in the support. The catalysts containing Ir (3.0% F) and PtU (3.0% F) exhibit some hydroisomerization activity to methylcyclopentane. However, inclusion of chlorine reduces the activity of PtIr whereas both chlorine and fluorine reduce the activity of PtRh-containing catalysts. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Cyclohexane; Dehydrogenation; Noble metals/Al_2O_3; Halogen promotion

1. Introduction

The dehydrogenation of cyclohexane on transition metals has drawn much attention, because of its very technological importance in petroleum refining and reforming processes [1]. Dehydrogenation of cyclohexane produces benzene which either desorbs or further decomposes to form graphitic carbon [2]. Cyclohexane dehydrogenation is a promising process by which the thermochemical concept can be demonstrated on a commercial scale [3]. In the hydroconversion of cyclohexane to benzene on Pt catalyst, cyclohexene has been suggested as an intermediate but it has never been directly detected [1,4–12]. However, the first direct observation of cyclohexene as an intermediate in this reaction has been achieved by Land et al. [13]. In addition, a second intermediate which is believed to be a bis(alkylidene) species is also detected. The reaction is studied as a function of temperature and time by laser-induced thermal desorption and Fourier transform mass spectrometry. The dehydrogenation of cyclohexane is the rate determining step in the reaction [4].

The dispersion of metal on the surface of the support is an important factor in determining catalytic

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activity and selectivity [14–18]. The dehydrogenation rate increases as the dispersion increases [19]. Okuhara et al. [20,21] investigated the effect of Ru dispersion and residual Cl of Ru/Al_2O_3 on the catalytic activity and selectivity of cyclohexane. They found that the dispersion and the residual Cl were the crucial factors controlling both activity and selectivity. Van Tiep et al. [22] found that chlorine remains on the support affecting both acidity and the selectivity of the catalyst.

The aim of this study is to find a better modification for the bifunctional catalyst (Pt/Al_2O_3) to improve its activity for hydroconversion of cyclohexane. To realize this goal, our study has been directed to investigate:

1. The effect of adding a second metal, Ir, Rh, Re or U, on the catalytic activity of Pt/Al_2O_3 catalyst.
2. The role of chlorination and fluorination on the catalytic activities of the catalysts.

2. Experimental

2.1. Catalyst preparation

Ten grams of γ-Al_2O_3 produced by "Rhone Poulenc-Chimie Fine" with the following specifications: white extrudates (2.5×3–5 mm); surface area, 216 m^2 g^{-1}, grain density 1.24 g cm^{-2}, structural density 3.0 g cm^{-3} and total pore volume 0.47 cm^3 g^{-1}, were impregnated in an aqueous solution of hexachloroplatinic acid, 0.019 M, such as to obtain a catalyst containing 0.35% Pt/γ-Al_2O_3. Citric acid was added to the platinum precursor solution to improve the penetration and dispersion of Pt into the catalyst pores [23,24]. After drying, the catalyst was calcined in air atmosphere at 530°C for 4 h. Reduction of the catalyst was then carried out in a flow of dry hydrogen (20 cm^3 min^{-1}) for 8 h in situ at 500°C. The same procedure was repeated for the preparation of 0.35% Ir/Al_2O_3, 0.35% Rh/Al_2O_3, 0.35% Re/Al_2O_3 and 0.35% U/Al_2O_3 using the precursors 0.033 M iridium chloride, 0.038 M rhodium chloride, 0.037 M ammonium perrhenate and 0.02 M uranyl nitrate, respectively.

Two grams of 0.35% Pt/Al_2O_3 was impregnated in a solution containing the required quantity of the precursor of the second metal, i.e., 0.35% (Ir, Rh, Re and U) [25]. The produced catalysts were then dried, calcined and reduced as mentioned above.

For promotion with Cl^- and F^- ions, ammonium chloride and ammonium fluoride, respectively, were added in the impregnation solutions. The required quantities of these salts were dissolved in distilled water to produce catalysts containing 1, 3 and 6 wt% of Cl or F. Drying was carried out very slowly in order to prevent removal of Cl or F. Then the catalysts were calcined and reduced as discussed above.

The dispersion of the metals with catalysts under study was determined using a pulsed technique of hydrogen chemisorption, based on 1:1 stoichiometry (H/M) according to Freel [26]. The data obtained are given in Table 1).

2.2. Dehydrogenation reactor, conditions and analysis

A micro-catalytic stainless steel reactor of 10 cm length and 6 mm external diameter was used. The catalyst bed contains 0.2 g of a catalyst in an internal stainless steel tube inserted into the micro-catalytic reactor. The reactor was electrically heated and electronically thermostated to ±1.0°C. The microreactor was fixed at the inlet of a gas chromatograph type 3400 Varian for direct analysis of the reaction effluents using a separation column of 4 m length packed with 10% didecylphthalate supported on chromosorb W-HP of 80–100 mesh. The reaction conditions were as follows: reaction temperature 200–500°C, flow rate of H_2 ~20 cm^3 min^{-1} and reactant pulse=1 μl.

3. Results and discussion

3.1. Dehydrogenation of cyclohexane over alumina-supported monometallic catalysts

Fig. 1 shows that the activities of all catalysts containing 0.35% of each metal increase with reaction temperature, following the order:

$$Pt > Rh > Ir > Re \geq U.$$

Above 425°C it is observed that the activity of Rh/Al_2O_3 catalyst slows down due to the significant hydrogenolysis of cyclohexane to propane which

Table 1
Hydrogen chemisorption parameters and dispersion values of the metal supported on alumina

No.	Catalysts	ν_H (cm^3)	Metal dispersion	Metal area ($m^2 g^{-1}$)
Monometallic				
1	0.35% Pt/Al_2O_3	0.282	0.70	0.908
2	0.35% Pt (3.0% Cl)/Al_2O_3	0.322	0.80	1.038
3	0.35% Pt (3.0% F)/Al_2O_3	0.346	0.86	1.116
4	0.35% Ir/Al_2O_3	0.277	0.68	0.895
5	0.35% Ir (3.0% Cl)/Al_2O_3	0.318	0.78	1.027
6	0.35% Ir (3.0% F)/Al_2O_3	0.318	0.78	1.027
7	0.35% Rh/Al_2O_3	0.511	0.67	1.647
8	0.35% Rh (3.0% Cl)/Al_2O_3	0.602	0.79	1.942
9	0.35% Rh (3.0% F)/Al_2O_3	0.549	0.72	1.770
Bimetallic				
1	0.35% Pt–0.35% Ir/Al_2O_3	0.263	0.65	0.849
2	0.35% Pt–0.35% Ir (3.0% Cl)/Al_2O_3	0.235	0.58	0.758
3	0.35% Pt–0.35% Ir (3.0% F)/Al_2O_3	0.304	0.75	0.980
4	0.35% Pt–0.35% Rh/Al_2O_3	0.347	0.66	1.120
5	0.35% Pt–0.35% Rh (3.0% Cl)/Al_2O_3	0.326	0.62	1.052
6	0.35% Pt–0.35% Rh (3.0% F)/Al_2O_3	0.305	0.58	0.984
7	0.35% Pt–0.35% Re/Al_2O_3	0.263	0.64	0.849
8	0.35% Pt–0.35% Re (3.0% Cl)/Al_2O_3	0.280	0.68	0.903
9	0.35% Pt–0.35% Re (3.0% F)/Al_2O_3	0.296	0.72	0.955
10	0.35% Pt–0.35% U/Al_2O_3	0.225	0.62	0.724
11	0.35% Pt–0.35% U (3.0% Cl)/Al_2O_3	0.250	0.69	0.807
12	0.35% Pt–0.35% U (3.0% F)/Al_2O_3	0.235	0.65	0.760

reaches 29.2% at 500°C (Table 2). The hydrogenolysis activity of Rh is indicated in previous studies [27–29] to be due to the higher percentage of d-bond character of Rh. On the other hand, Re- and U-supported γ-Al_2O_3 have negligible dehydrogenation activities.

3.2. Dehydrogenation activity of bimetallic catalysts

The effect of addition of 0.35 wt% of Ir, Rh, Re or U together with 0.35% Pt on γ-alumina support for the dehydrogenation of cyclohexane has been investigated. It is found that by introducing a second metal,

Table 2
Product distribution for the hydroconversion of cyclohexane over Rh/Al_2O_3 catalyst at different reaction temperatures

Component in product	Temperature (°C)												
	200	225	250	275	300	325	350	375	400	425	450	475	500
Propane	0.0	0.0	0.0	0.1	0.4	1.1	3.2	9.0	15.7	22.7	26.4	26.8	29.2
Benzene	0.0	0.1	0.7	3.6	8.4	13.1	18.4	21.7	24.1	27.4	28.7	30.6	31.4

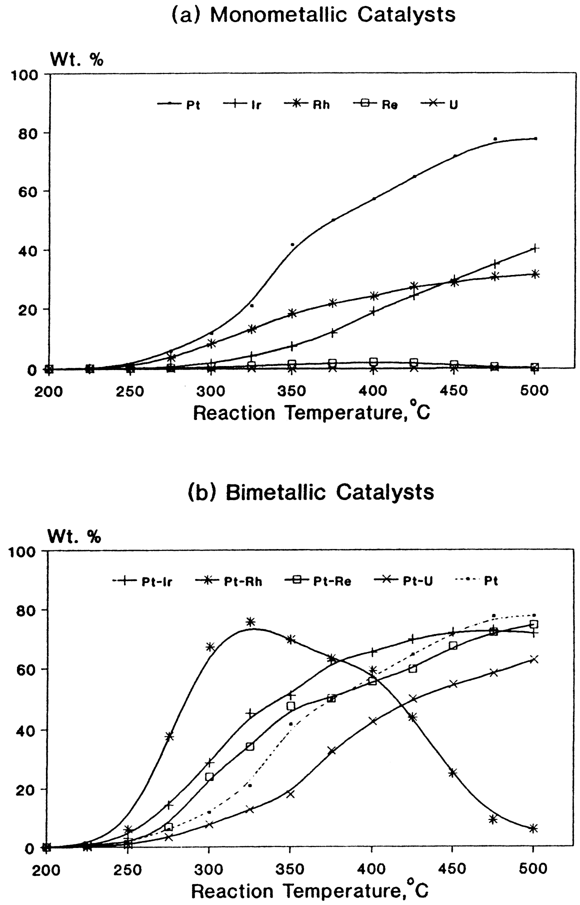

Fig. 1. Conversion of cyclohexane over monometallic (a) and bimetallic (b) catalysts.

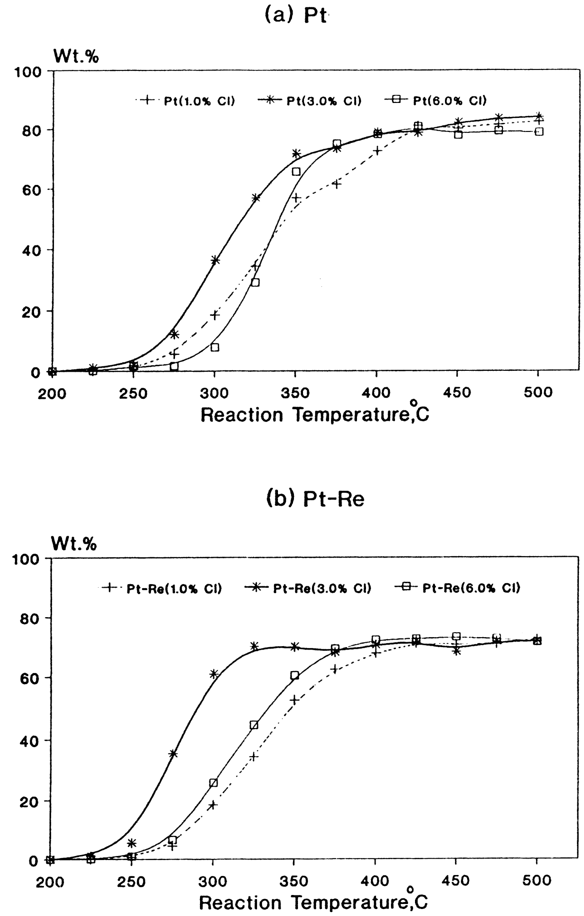

Fig. 2. Conversion of cyclohexane over (a) Pt/Al_2O_3 and (b) Pt–Re/Al_2O_3 catalysts with different chlorine content.

the activity of Pt is enhanced (Fig. 2). The activity increases as a function of reaction temperature between 225°C and 350°C following the order:

PtRh > PtIr > PtRe > Pt > PtU.

At higher reaction temperatures (>350°C) the rate of dehydrogenation decreases on PtRh due to the enhanced hydrogenolysis of cyclohexane to propane. Patent literature discloses the use of Rh together with Pt in commercial naphtha reforming catalysts by virtue of its higher dehydrogenation activity [30,31]. However, the activities of PtRe and PtIr catalysts exceed that of Pt alone up to 400°C, beyond which the activity of PtIr surpasses that of PtRe. However, above 450°C the monometallic Pt catalyst is more active than $PtIr/Al_2O_3$ catalyst.

On the other hand, the addition of U to Pt reduces its dehydrogenation activity. This may be attributed to the low electronegativity of U (1.38) compared with that of Pt (2.28) which leads to the formation of $Pt^{\delta-}$ and $U^{\delta+}$.

It is known that γ-Al_2O_3 supported PtRe and PtIr are most frequently used as commercial naphtha reforming catalysts.

3.3. Effect of halogenation with varying contents of Cl or F on the activity of γ-alumina supported Pt and PtRe catalysts for cyclohexane dehydrogenation

3.3.1. Effect of chlorine content

It is found (Fig. 2(a) and (b)) that 3% chlorine is the optimum for enhancing the dehydrogenation of cyclo-

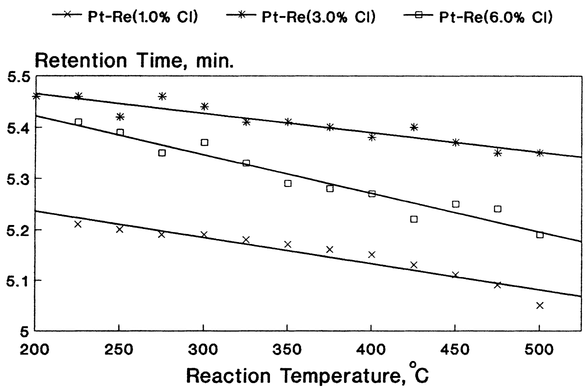

Fig. 3. Retention time of produced benzene over Pt–Re/Al_2O_3 catalysts with different chlorine contents.

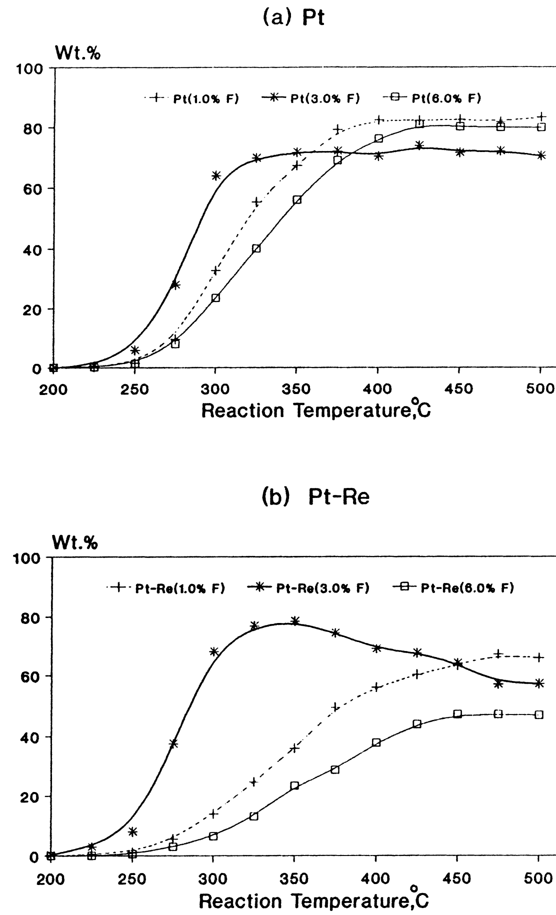

Fig. 4. Conversion of cyclohexane over (a) Pt/Al_2O_3 and (b) Pt–Re/Al_2O_3 catalysts with different fluorine content.

hexane over Pt and PtRe catalysts. This may be attributed to improved hydrogen spillover [32–34]. At higher reaction temperatures (>400°C) the dehydrogenation activities of the two catalysts become almost equal irrespective of the chlorine content and temperature.

The gas chromatographic retention times measured for benzene on the chlorinated catalysts under study (Fig. 3) can be arranged according to their Cl content in the order: 3%>6%>1%.

The catalyst containing 3% Cl appears to adsorb the produced benzene more strongly than 1.0% and 6.0% Cl-containing catalysts which inhibit further cyclohexane molecules to be adsorbed.

3.3.2. Effect of fluorine content

Fig. 4(a) and (b) shows that 3% F Pt/Al_2O_3 and 3% F PtRe/Al_2O_3 catalysts are more active for cyclohexane dehydrogenation than those containing 1.0% and 6.0% F, which can be attributed to higher hydrogen spillover by analogy to the 3.0% chlorinated catalyst [32–34]. It has been pointed out that F increases both Brønsted and Lewis acidity [35–38]. At low F content, the number of Brønsted sites increases to a certain limit beyond which it decreases with further increase of F [39–41]. The declination observed in cyclohexane dehydrogenation on the 3% F PtRe/Al_2O_3 catalyst beyond 350°C, and the relatively lower unchanged activity using 3% F Pt/Al_2O_3 can be attributed to retarded adsorption of the benzene molecules produced, since the higher acidity of the catalyst increases the adsorption of benzene, which is relatively more basic among other hydrocarbons.

The retention times of benzene in its gas chromatograms run at varying temperatures using the catalysts under study with F contents of 1.0%, 3.0% and 6.0% are given in Fig. 5. The highest retention times are obviously obtained on the 3.0% F-containing catalyst, which may support the above finding.

Lower and higher contents than 3.0% F are found to give lower activities for cyclohexane dehydrogenation. High F contents are assumed [42–44] to result in the formation of aluminum fluoride and aluminum hydroxy-fluorides which have been found to decrease the surface area of the support as well as to decrease the metal dispersion in the support [45].

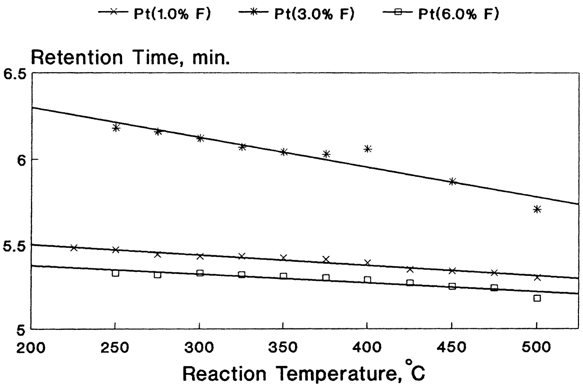

Fig. 5. Retention time of produced benzene over Pt/Al_2O_3 catalysts with different fluorine content.

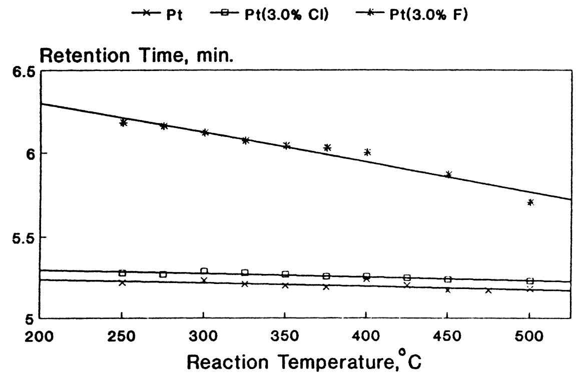

Fig. 7. Retention time of produced benzene over non-halogenated and 3.0% halogenated Pt/Al_2O_3 catalysts.

3.4. *Effect of 3.0% halogen on the dehydrogenation activities of the monometallic catalysts*

3.4.1. *0.35% Pt/Al_2O_3 catalyst*

Comparing the catalytic dehydrogenation activities of the halogenated and non-halogenated Pt/Al_2O_3 catalysts in the temperature range 275–325°C, it is observed that conversion of cyclohexane to benzene is in the range 5.9–20.9%, 12.2–56.8% and 27.9–69.8% on Pt/Al_2O_3, $Pt(Cl)/Al_2O_3$ and $Pt(F)/Al_2O_3$ catalysts, respectively (Fig. 6). This enhancement of the dehydrogenation activity can be attributed to the improved dispersion of Pt on supported alumina. Table 1 shows that Pt dispersion amounts to 0.70, 0.80 and 0.86 for these catalyst, respectively. Dehydrogenation of cyclohexane on the fluorinated catalyst reaches a maximum value at 325°C and remains nearly constant till 500°C. However, the activity of the chlorinated catalyst has exceeded that of the fluorinated catalyst at >350°C, which may be attributed to the relatively stronger adsorption of the product, benzene, on the fluorinated catalyst (as evident from the retention time of benzene, Fig. 7) than on the chlorinated catalysts. It is reported that fluorine treatment increases the acidic character than chlorine treatment [38]. The inhibition at higher conversion by the aromatic product accumulation has been observed in a similar study [46].

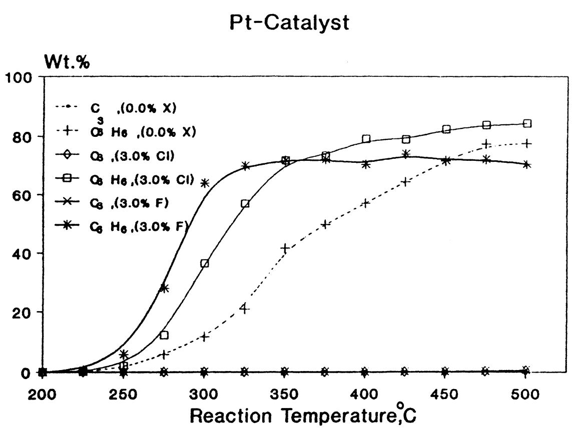

Fig. 6. Conversion of cyclohexane over non-halogenated and 3.0% halogenated Pt/Al_2O_3 catalysts.

3.4.2. *0.35% Ir/Al_2O_3 catalyst*

It is found that chlorination of the 0.35% Ir/Al_2O_3 catalyst is more effective for enhancing the dehydrogenation activity of cyclohexane to benzene than does a corresponding treatment with fluorine (Fig. 8(a)). This can be attributed to enhancing competitive hydroisomerization of cyclohexane to methylcyclopentane which reaches a maximum of 8.7% at 350°C, then declines to a minimum at 500°C, whereas the dehydrogenation reaction increases to 19.0% at this temperature. The observed hydroisomerization activity to methylcyclopentane may be due to the pronounced acidity of the flourinated alumina [43]. Moreover, this unique behaviour requires a balance between both metal and acid sites needed for isomerization [47].

On the other hand, the halogenated catalysts show moderate hydrocracking activity which reaches a

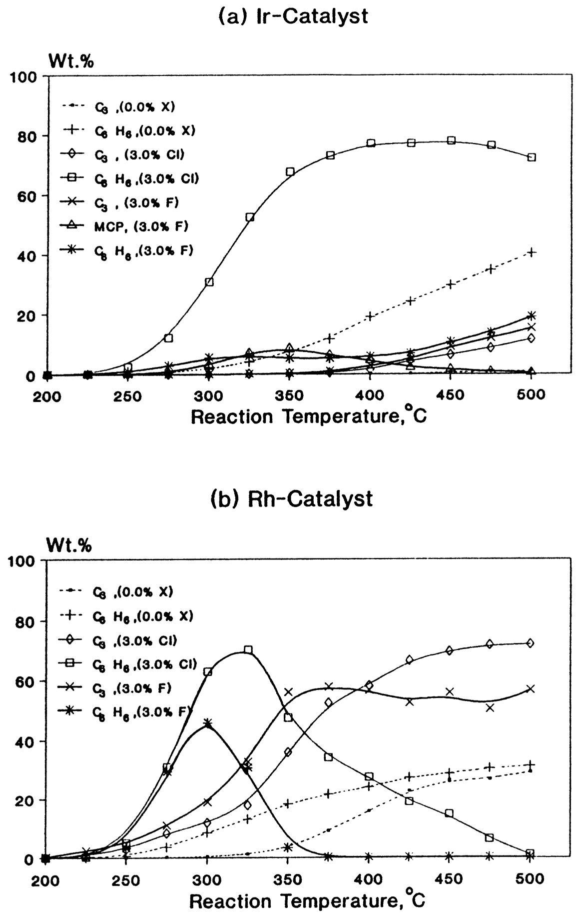

Fig. 8. Conversion of cyclohexane over non-halogenated and 3.0% halogenated (a) Ir/Al_2O_3 and (b) Rh/Al_2O_3 catalysts.

maximum value of 15.2% at 500°C over the $Ir(F)/Al_2O_3$ catalyst. This hydrocracking activity of both halogenated catalysts may be due to the pronounced acidity created by halogenation, compared to the non-halogenated catalysts [35–37,48,49]. Hydrocracking requires catalysts containing strong acid sites with a well-dispersed metal [45].

3.4.3. 0.35% Rh/Al_2O_3 catalyst

Fig. 8(b) shows that the dehydrogenation activity of Rh/Al_2O_3 catalyst increases gradually with reaction temperature to reach 31.4% at 500°C. However, the activities of the halogenated catalysts increases sharply with reaction temperature till reaching a maximum then decreases with further increase in temperature. Such a behaviour can be explained in terms of enhanced hydrogenolysis of cyclohexane to propane, which requires strong acid sites and well-dispersed metal [45]. By comparing the two maxima it is observed that the more dispersed $Rh(Cl)/Al_2O_3$ catalyst has a higher activity relative to $Rh(F)/Al_2O_3$ (Table 1).

The hydrogenolysis activity of both halogenated catalysts increases with increasing temperature to reach a maximum value of 55.8% at 350°C on the $Rh(F)/Al_2O_3$ catalyst and 72.1% at 500°C on the $Rh(Cl)/Al_2O_3$ catalyst. However, the non-halogenated catalyst exhibits a moderate activity of about half that of fluorinated catalyst at 500°C, due to its poor acidic character relative to both halogenated catalysts [38,48,49]. On the other hand, Re/Al_2O_3 and U/Al_2O_3 exhibit negligible activities, whether halogenated or not, for the dehydrogenation of cyclohexane up to 500°C.

3.5. Effect of 3.0% halogen on the dehydrogenation activities of the bimetallic catalysts

3.5.1. $PtIr/Al_2O_3$ and $PtRh/Al_2O_3$ catalysts

3.5.1.1. Effect of chlorine. Fig. 9(a) and (b) shows that chlorine reduces the activities of dehydrogenation and hydrogenolysis of cyclohexane as compared to the non-halogenated catalysts. This may be attributed to transforming the metal atoms; Pt, Ir and Rh at the interface to the ionic form by their interaction with chlorine. This conclusion is also withdrawn in previous studies by Okuhara et al. [21], who conclude that, during the hydroconversion of cyclohexane over chlorinated Ru/Al_2O_3, the formation of $Ru^{\delta+}$ at the interface takes place, over which benzene is strongly adsorbed due to its relative basicity. Also, Birke et al. [50], from their study on the effect of chlorine on the surface properties of $PtIr/Al_2O_3$ catalyst, conclude the existence of $PtCl_2$ and $IrCl_3$ at 300–450°C. Moreover, the observed decrease in activity of cyclohexane hydroconversion after chlorine treatment may be attributed to the decrease of metal dispersion in case of PtIr- and PtRh-containing catalysts as is evident from Table 1.

3.5.1.2. Effect of fluorine. Fig. 9(a) shows that fluorine enhances both dehydrogenation and hydro-

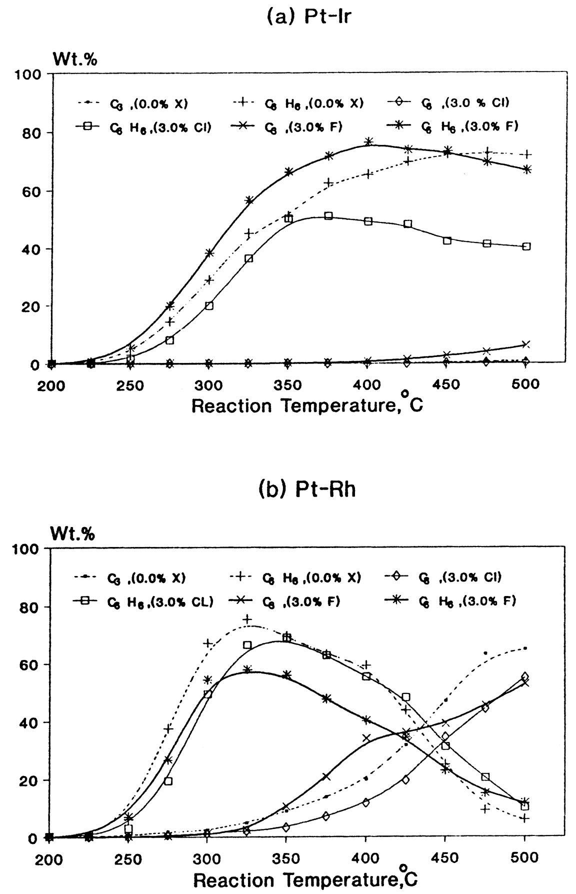

Fig. 9. Conversion of cyclohexane over non-halogenated and 3.0% halogenated (a) Pt–Ir/Al_2O_3 and (b) Pt–Rh/Al_2O_3 catalysts.

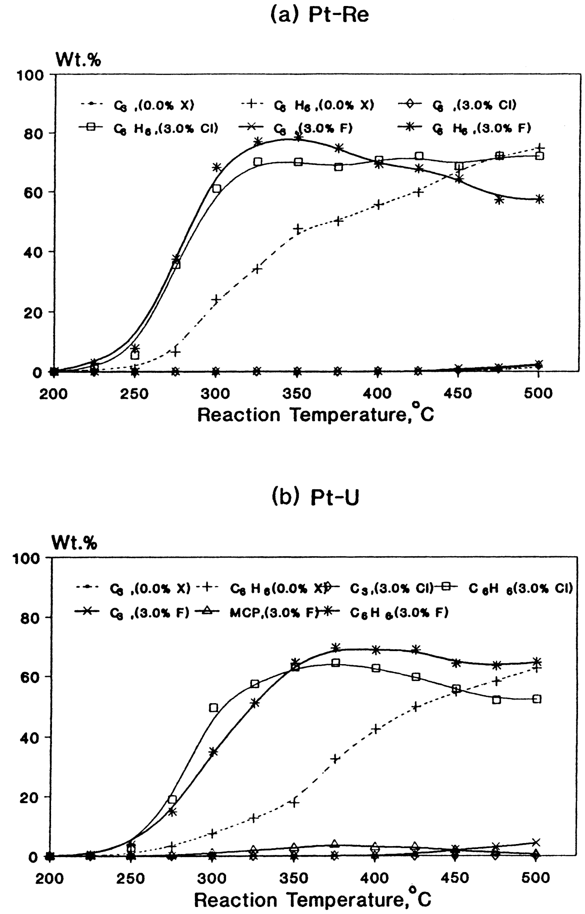

Fig. 10. Conversion of cyclohexane over non-halogenated and 3.0% halogenated (a) Pt–Re/Al_2O_3 and (b) Pt–U/Al_2O_3 catalysts.

genolysis of cyclohexane over PtIr/Al_2O_3 up to 450°C, beyond which the dehydrogenation activity decreases. This effect can be attributed to (a) an improved dispersion of the metal on the support (Table 1), and (b) stronger acid sites are formed during the fluorination of γ-Al_2O_3 [51–53] upon which cyclohexane adsorption increases, thus increasing dehydrogenation to benzene. It has been reported that both strong acid sites and high metal dispersion are necessary for active hydrogenolysis [45]. On the other hand, inclusion of fluorine in the PtRh/Al_2O_3 catalyst is found to reduce both dehydrogenation and hydrogenolysis (Fig. 9(b)). The significant decrease of benzene and propane production can be attributed, as mentioned before, to the enhanced adsorptivity of produced benzene and to the relatively poor metal dispersion (Table 1).

3.5.2. *PtRe/Al_2O_3 catalyst*

It is observed in Fig. 10(a) that maximum conversion to benzene reaches 34.1%, 70.1% and 77.0% at 325°C on alumina-supported PtRe, PtRe(Cl) and PtRe(F), respectively. This significant promotion effect by halogen can be attributed to improved dispersion of Pt and Re on the support (Table 1). Above 350°C, the dehydrogenation of cyclohexane on chlorinated PtRe/Al_2O_3 remains almost unchanged, whereas on fluorinated PtRe/Al_2O_3, the activity decreases gradually till 500°C. This may be attributed to the relatively stronger adsorption of benzene which retards further dehydrogenation of cyclohexane.

3.5.3. PtU/Al_2O_3 catalyst

Fig. 10(b) shows that the dehydrogenation activity increases by treatment of the PtU/Al_2O_3 with halogen up to 350°C, then slows down. Above 375°C, it starts to decrease and reach a constant value, 53.2% in the presence of Cl and 64.1% in the presence of fluorine, at about 450°C. The decrease in activity can be attributed to benzene adsorption as mentioned before. However, at lower reaction temperatures, the catalyst shows a relatively higher activity as a result of chlorine treatment compared with fluorine treatment. This may be due to the relative high metal dispersion assisted by chlorine (Table 1). On the other hand, the fluorine promoted catalyst exhibits, in addition, poor isomerization and hydrocracking activity.

3.6. Apparent reaction rates and apparent activation energies

According to Bassett and Habgood [54] the apparent reaction rate constant, kK, for first-order pulsed systems is given in the following equation:

$$kK = \frac{F^{\circ}}{273RW} \ln \frac{1}{1-X}, \qquad (1)$$

where k is the reaction rate constant, K the adsorption equilibrium constant, F° the flow rate of the carrier at NTP, R the gas constant, W the catalyst weight and X is the mole fraction converted.

In the present study, the catalytic activity is calculated relative to the metal surface area, S_a, as shown in the following equation:

$$kK = \frac{F^{\circ}}{273RS_a} \ln \frac{1}{1-X}. \qquad (2)$$

The values of kK thus obtained are given in Tables 3 and 4 for the monometallic and bimetallic catalysts, respectively.

The data in Table 3 show that, in general, the fluorinated Pt/Al_2O_3 catalyst is the most active among the monometallic catalysts under study, during the lower temperature range (250–325°C). However, during the higher temperature range (350–500°C) the chlorinated Pt/Al_2O_3 catalysts gives highest kK values.

Among the bimetallic catalysts studied, the PtRe(F)/Al_2O_3 catalyst gives highest kK value at temperatures of 250–350°C. However, it appears interesting to point out that the corresponding PtRe(Cl)/Al_2O_3 catalyst can be considered as the second in activity following the PtRe(F)/Al_2O_3 catalyst during the lower temperature range, but still possessing higher activity than this catalyst during the higher temperature range. From an economic point of view, dehydrogenation at lower temperatures is of highest interest since this reaction is endothermic and the use of lower temperatures will thus protect the catalyst from coke deactivation as well as from premature aging.

The apparent activation energy, E_a, can be calculated from the slope of a plot of ln kK vs. $1/T$ [54]. The values of E_a thus obtained are given in Table 5.

Table 3
Apparent reaction rate constant, kK, for cyclohexane dehydrogenation on monometallic catalysts at different reaction temperatures

Catalysts	$kK \times 10^6$ (mol atm^{-1} $g_{m^2}^{-1}$ s^{-1})										
	Temperature (°C)										
	250	275	300	325	350	375	400	425	450	475	500
0.35% Pt/Al_2O_3	0.20	1.51	2.03	3.84	8.82	11.21	13.82	16.90	20.60	24.40	24.51
0.35% Pt (3.0% Cl)/Al_2O_3	0.28	1.87	6.47	12.00	18.03	19.03	22.30	22.30	24.71	25.91	26.40
0.35% Pt (3.0% F)/Al_2O_3	0.82	4.36	13.60	16.01	16.80	17.00	16.25	17.91	16.81	17.01	16.32
0.35% Ir/Al_2O_3	0.02	0.10	0.30	0.70	1.28	2.92	3.53	4.63	5.86	7.12	8.58
0.35% Ir (3.0% Cl)/Al_2O_3	0.37	1.87	5.32	10.70	16.31	18.91	21.31	21.31	21.81	20.91	18.51
0.35% Ir (3.0% F)/Al_2O_3	0.13	0.41	0.82	0.91	0.97	0.97	0.88	1.05	1.64	2.15	3.05
0.35% Rh/Al_2O_3	0.06	0.33	0.79	1.27	1.83	2.21	2.48	2.89	3.05	3.30	3.40
0.35% Rh (3.0% Cl)/Al_2O_3	0.39	2.84	7.58	9.28	4.93	3.21	2.47	1.62	1.22	0.50	0.08
0.35% Rh (3.0% F)/Al_2O_3	0.27	2.94	5.14	3.09	0.03	0.01	0.01	0.01	0.01	0.01	0.01

Table 4
Apparent reaction rate constant, *kK*, for cyclohexane dehydrogenation on bimetallic catalysts at different reaction temperatures

Catalysts	$kK \times 10^6$ (mol atm^{-1} g$_{m^2}^{-1}$ s^{-1})										
	Temperature (°C)										
	250	275	300	325	350	375	400	425	450	475	500
0.35% Pt–0.35% Ir/Al_2O_3	0.53	2.75	5.96	10.60	12.61	17.21	18.60	20.90	22.42	22.82	22.11
0.35% Pt–0.35% Ir (3.0% Cl)/Al_2O_3	0.24	1.64	4.33	8.86	13.71	14.03	13.32	12.90	10.81	10.40	10.11
0.35% Pt–0.35% Ir (3.0% F)/Al_2O_3	0.79	3.32	7.31	12.60	16.52	19.13	21.91	20.20	20.11	17.92	16.71
0.35% Pt–0.35% Rh/Al_2O_3	0.82	3.55	14.81	18.74	15.82	13.33	11.94	7.66	3.83	1.25	0.79
0.35% Pt–0.35% Rh (3.0% Cl)/Al_2O_3	0.42	3.05	9.59	15.50	16.64	13.93	11.45	9.28	5.29	3.22	1.48
0.35% Pt–0.35% Rh (3.0% F)/Al_2O_3	0.90	4.76	11.85	13.08	12.33	9.75	7.78	6.43	3.95	2.44	1.85
0.35% Pt–0.35% Re/Al_2O_3	0.18	1.22	4.82	7.32	11.33	12.24	14.22	15.95	19.60	22.31	24.05
0.35% Pt–0.35% Re (3.0% Cl)/Al_2O_3	0.93	7.23	16.30	19.92	19.84	18.85	20.12	20.81	18.93	20.90	20.90
0.35% Pt–0.35% Re (3.0% F)/Al_2O_3	1.28	7.43	18.32	22.81	23.90	21.33	18.31	17.64	16.05	13.22	13.22
0.35% Pt–0.35% U/Al_2O_3	0.14	0.67	1.60	2.77	4.03	8.14	11.42	14.12	16.20	17.92	20.32
0.35% Pt–0.35% U (3.0% Cl)/Al_2O_3	0.52	3.89	12.61	15.70	17.32	19.11	18.14	16.73	14.92	13.52	13.61
0.35% Pt–0.35% U (3.0% F)Al_2O_3	0.76	3.14	8.51	14.05	20.22	23.21	22.70	22.81	20.42	19.71	20.40

Table 5
Apparent activation energies for cyclohexane dehydrogenation on monometallic and bimetallic catalysts

No.	Catalysts	E_a (kJ mol^{-1})	
		In lower temperature region	In higher temperature region
Monometallic			
1	0.35% Pt/Al_2O_3	86.78	31.60
2	0.35% Pt (3.0% Cl)/Al_2O_3	125.52	14.64
3	0.35% Pt (3.0% F)/Al_2O_3	127.07	–
4	0.35% Ir/Al_2O_3	98.03	38.07
5	0.35% Ir (3.0% Cl)/Al_2O_3	119.54	20.08
6	0.35% Ir (3.0% F)/Al_2O_3	96.79	55.77
7	0.35% Rh/Al_2O_3	89.66	19.46
8	0.35% Rh (3.0% Cl)/Al_2O_3	142.26	–
9	0.35% Rh (3.0% F)/Al_2O_3	143.47	–
Bimetallic			
1	0.35% Pt–0.35% Ir/Al_2O_3	102.09	23.85
2	0.35% Pt–0.35% Ir (3.0% Cl)/Al_2O_3	123.05	–
3	0.35% Pt–0.35% Ir (3.0% F)/Al_2O_3	115.06	29.29
4	0.35% Pt–0.35% Rh/Al_2O_3	122.51	–
5	0.35% Pt–0.35% Rh (3.0% Cl)/Al_2O_3	144.35	–
6	0.35% Pt–0.35% Rh (3.0% F)/Al_2O_3	140.16	–
7	0.35% Pt–0.35% Re/Al_2O_3	135.14	29.41
8	0.35% Pt–0.35% Re (3.0% Cl)/Al_2O_3	155.64	–
9	0.35% Pt–0.35% Re (3.0% F)/Al_2O_3	144.35	–
10	0.35% Pt–0.35% U/Al_2O_3	98.32	28.87
11	0.35% Pt–0.35% U (3.0% Cl)/Al_2O_3	133.34	–
12	0.35% Pt–0.35% U (3.0% F)/Al_2O_3	156.90	–

It is evident from Table 5 that the incorporation of Cl or F in catalysts containing a single metal or a couple of the metals, under study, on a γ-alumina support, gives an increase in the apparent activation energy for cyclohexane dehydrogenation. However, Cl incorporation produces a higher increase of E_a than F, except for the PtU/Al_2O_3 catalyst, where E_a for the reaction on PtU(F)/Al_2O_3 (156.90 kJ mol^{-1}) exceeds that on the PtU(Cl)/Al_2O_3 (133.34 kJ mol^{-1}). Such a discrepancy may be due to the fact that U is the only rare earth metal under study, and thus gives a different behaviour by its coupling with Pt. Uranium is an actinide with lower electronegativity.

However, it is to be pointed out that F incorporation in Ir/Al_2O_3 and PtRh/Al_2O_3 catalysts, as well as Cl incorporation in PtIr/Al_2O_3 and PtRh/Al_2O_3 catalysts give negative response (inhibition) on the dehydrogenation activities, although the activation energies obtained using the Cl and F incorporating catalysts are invariably higher on the Cl-containing than the F-containing catalyst (Table 5). Such a behaviour may be attributed to preserving the original texture of the catalyst unaltered. For instance, some Pt, Ir and Rh atoms in the catalysts may be transformed at the interface to ionic forms by interaction with halogen. However, their metal dispersion is also affected (Table 1).

However, during the higher reaction temperature region, E_a can be estimated (with lower magnitudes) for some catalysts, e.g., the unhalogenated catalysts: Pt/Al_2O_3, Ir/Al_2O_3, Rh/Al_2O_3, PtIr/Al_2O_3, PtRe/Al_2O_3 and PtU/Al_2O_3. These E_a values indicate, in most cases, significant diffusion restriction. Furthermore, the highest temperature activities of most catalysts incorporating Cl or F, are unaffected by a further increase of reaction temperature which indicates that benzene concentration on the catalyst surface, reaches a state of equilibrium and the number of newly adsorbed cyclohexane molecules is limited by the number of strongly adsorbed benzene (more polar) produced.

4. Conclusion

The following conclusion can be drawn from the data obtained:

1. Most of the catalysts under study enhance cyclohexane dehydrogenation up to 350°C beyond which the activity may not improve via further increase of temperature or even decline. This may be attributed to the stronger adsorption of the produced benzene molecules, thus retarding further cyclohexane adsorption and reactin.
2. Combination of Ir, Rh or Re with Pt enhances the catalytic activity, whereas U inhibits this activity.
3. Halogenation of the monometallic or bimetallic catalysts with chlorine or fluorine enhances the catalytic activity except for the catalysts containing Ir(F), PtIr(Cl), PtRh(Cl) and PtRh(F).
4. The optimum concentration of halogen for enhancing cyclohexane dehydrogenation is 3% by weight, which may be attributed to the increasing hydrogen spillover and improving the metal dispersion in the support.

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