

The Kinetics of Gas Phase Hydrogenation of Cyclohexene on Alumina-supported Platinum in Static Reactor¹

O. Zahraa, S.H. Al Khowaiter², and E. Ammar

Department of Chemistry, King Saud University,
P.O. Box 2455 Riyadh 11451, Kingdom of Saudi Arabia

ABSTRACT. The kinetics of cyclohexene hydrogenation over Pt-Al₂O₃ catalysts was investigated in a static reactor, between 303 and 373k, and hydrogen partial pressure from 40 to 220 torr, and cyclohexene partial pressure from 20 to 80 torr. Cyclohexane was the only product observed. The rate of hydrogenation (torr min⁻¹ g Pt⁻¹) exhibited a maximum at 160 torr of hydrogen. The reaction order with respect to hydrocarbon has been found slightly negative at low temperature, and about (0.5) at high temperature. The order with respect to hydrogen varied from (0.8) to (-1) as the pressure of hydrogen increased. The experimental results of this work implied that the hydrogenation on alumina-supported platinum proceeds via the associative mechanism.

The hydrogenation reaction is widely used to study the activity and kinetic behaviour of transition metals catalysts. The hydrogenation of benzene to cyclohexane was emphasized by many authors, (Franco and Phillips 1980, Dixon and Singh 1969). They reported reaction orders with respect to benzene and hydrogen at different temperatures and pressure ranges. Also, the activation energies for benzene hydrogenation were mentioned.

For cyclohexene hydrogenation, most of the works have been carried out in homogeneous system, (Taqi Khan, Mehreen, *et al.* 1981, Taqui Khan, Rafeeq, *et al.* 1981) and in liquid phase, (Tzinmann 1981). Other works, in gas phase, were also reported over palladium and nickel catalysts, (Yong Lee *et al.* 1981 and McConica 1982). Over platinum, Segal *et al.* (1978) have investigated the kinetic of

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2 Address for correspondence.

cyclohexene hydrogenation over platinum catalysts supported on silica gel; and Davis *et al.* (1982) have performed the hydrogenation of cyclohexene on single crystal of platinum. In this work, we report the study of the gas-phase hydrogenation of cyclohexene in a static reactor over platinum catalysts supported on γ -alumina.

Experimental

Catalysts

Platinum supported on γ -alumina was prepared by impregnating aqueous solutions of chloroplatinic IV acid 40% Pt on the support, according to the Ipatieff method (Pines *et al.* 1948). The concentration of Pt was varied from 0.2 to 2 wt %.

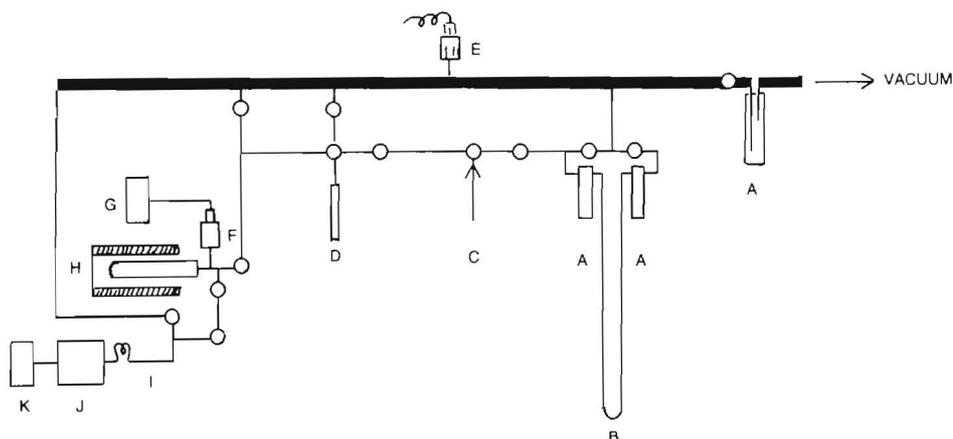
Catalysts Characterization

In order to determine the degree of dispersion of platinum, the adsorption of hydrogen was employed at 473 K in a volumetric glass system after the catalysts had been outgassed at 573 K under pressure of 10^{-5} torr for a period of four hours. A hydrogen adsorption isotherm was then measured according to the method used by Spendel and Boudart (1960) and Rizk (1975).

Catalytic Reaction

The gas-phase hydrogenation of cyclohexene was carried out by using the static reactor, a pyrex tubular vessel with a volume of about 100 ml containing the catalysts (0.05-0.25 g) spread uniformly along the 20 cm length of vessel, which was placed horizontally in a tube furnace. The furnace temperature was controlled by a continuous controller Witronic II, obtained from Philips, and the reactor was evacuated down to $\sim 10^{-5}$ torr by using a turbomolecular pump (PFEIFFER tsu 270) supplied by Balzers. A schematic diagram of the experimental apparatus is represented in Fig. 1.

The temperature was then fixed as desired (303-373 K). The cyclohexene was outgassed several times, and then transferred to the reaction vessel at the desired pressure (20-80 torr), the convenient pressure of hydrogen (40-220 torr) was then introduced to the reaction system, and the reactor isolated from the rest of the apparatus by a Teflon Tap. The decrease of pressure with time in the reactor, due to the hydrogenation of cyclohexene, was monitored continuously by a previously calibrated strain gauge, pressure transducer, and a chart recorder. The reaction products were injected into a Varian 3700 Gas Chromatograph, *via* a microvolume six ports sampling valve. The chromatographic column, 6 meters length of 5% didecylphthalate and 5% Bentone on chromosorb W-HP 80/100 mesh was used for analysis at 70°C. Only cyclohexane and cyclohexene were detected in the injected sample.



- | | |
|--------------------------------|---|
| A : Trap | G : Recorder |
| B : Manometer | H : Reaction vessel and tubular furnace |
| C : Gas inlet | I : Sample loop |
| D : Hydrocarbon inlet | J : G.C. |
| E : Pressure measurement gauge | K : Recorder integrator |
| F : Transducer | |

Fig. 1. Schematic diagram of static apparatus for kinetic studies

Materials

Chloroplatinic IV acid 40% Pt was obtained from Fluka, γ -Alumina from Merck, and cyclohexene puriss from Koch-Light Laboratories Ltd, and found chromatographically pure. Hydrogen (extra pure) was generated by hydrogen generator purchased from General Electric and was passed through silica gel and molecular-sieve traps.

Results and Discussion

The rate of hydrogenation of cyclohexene was studied with different catalysts prepared with variable platinum contents. At constant volume, the reaction occurs with pressure drop. The activity is expressed as the initial rate of hydrogenation measured by the slope $(-\Delta p / \Delta t)$ of the tangent to the pressure-time curve at $t = 0$, Fig. 2. The rate was then calculated per gramme of catalyst or gramme of platinum. The reaction mixture was analysed in order to determine the composition, the gas sample contained only cyclohexane and cyclohexene for all

runs at temperature less than 373 K. (benzene starts to appear above this temperature).

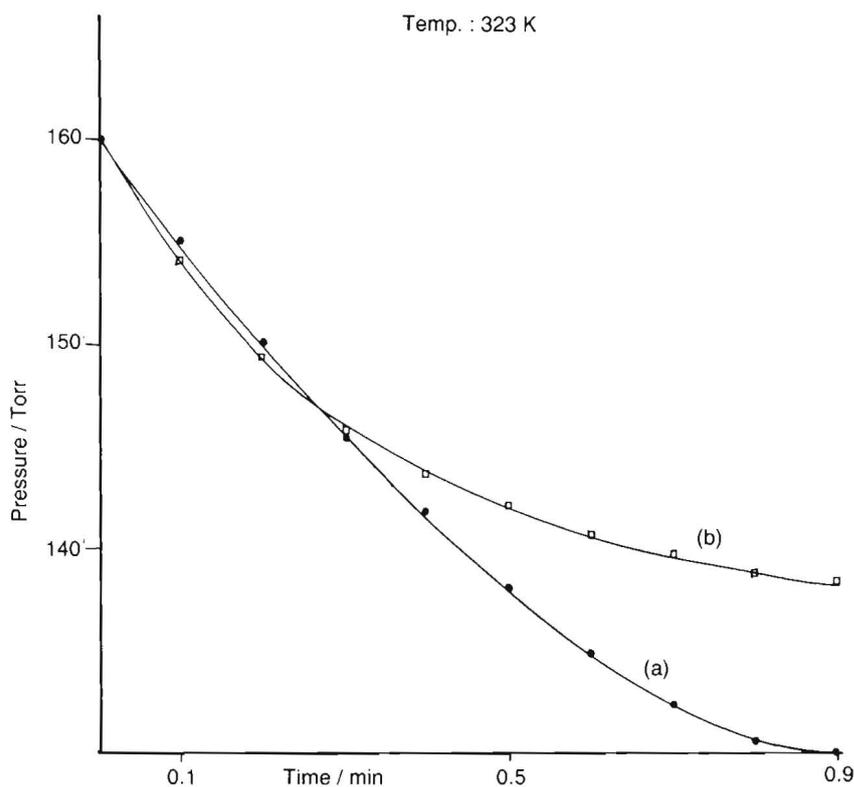


Fig. 2. Change of pressure with time during hydrogenation of cyclohexene on (a) 0.2% Pt/Al₂O₃ and (b) 2% Pt/Al₂O₃

The variation of catalytic activity, R (Torr min⁻¹ g/Pt⁻¹) at different temperatures for the hydrogenation of cyclohexene is shown in Fig. 3 for catalysts with different platinum contents. The decrease in the activity with an increase in the platinum content is more pronounced at high temperature. A similar change was also reported with palladium supported catalysts, (Yang Lee *et al.* 1981). The hydrogen chemisorption measurement (Sousi 1985) pointed out that the platinum atoms exposed on the surface per unit weight of metal changed with the amount of Pt content in the same manner as the activity.

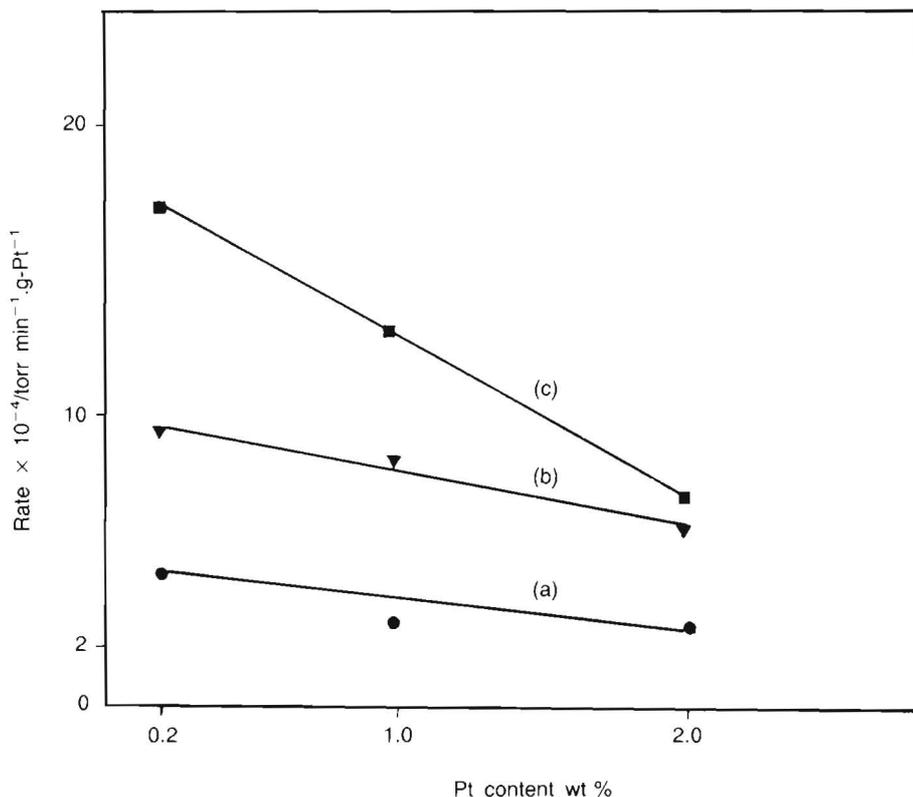


Fig. 3. Change in catalytic activity (rate) with Pt content, at (a) 303K, (b) 323K, (c) 348K

The variation in cyclohexene partial pressure was carried out at different temperature over 2% Pt/Al₂O₃ catalyst, while the partial pressure of hydrogen was kept constant. Figure 4 shows that, an increase in cyclohexene partial pressure at any particular temperature caused an increase in the activity, except at 303 K, where the activity is slightly decreased with the hydrocarbon partial pressure. It has been observed from previous experiments in the vapour-phase with Pt catalysts (Segal *et al.* 1978) and in the liquid-phase (Tinzmann 1981) with Ni catalysts that the activity of hydrogenation of cyclohexene remained constant when the partial pressure (or the concentration of olefin) changes at this temperature. The strong adsorption of cyclohexene on the surface of the catalyst might be considered to cause this phenomena.

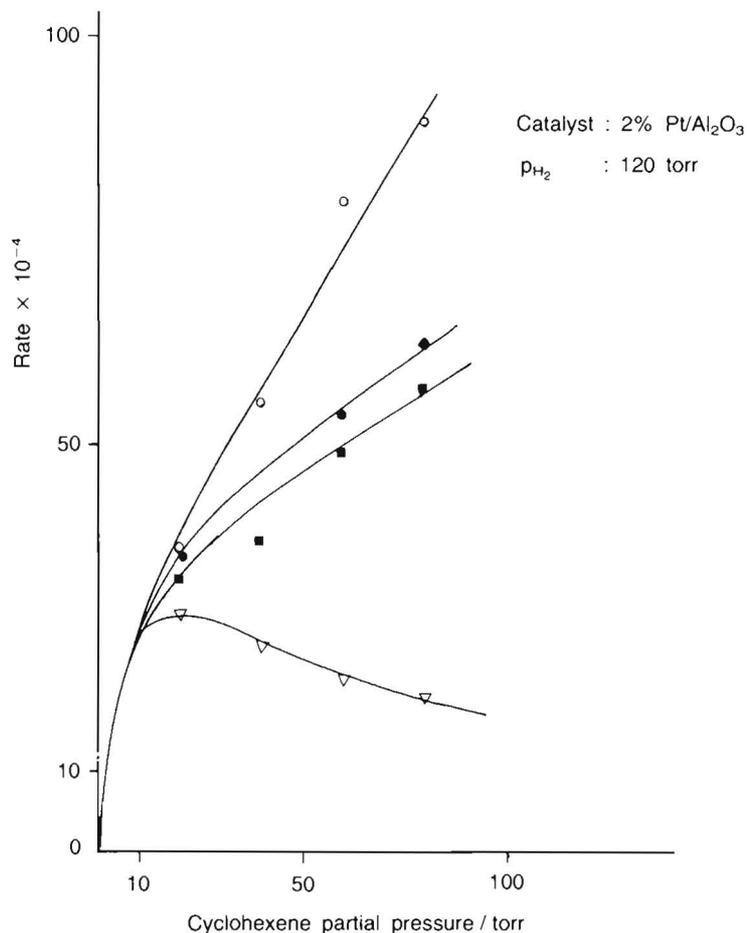


Fig. 4. Effect of the partial pressure of cyclohexene on the rate of hydrogenation (torr min⁻¹, g-Pt⁻¹).
 ▽ 303K; ● 323K; ○ 348K; ■ 373K

The influence of hydrogen partial pressure on the activity was studied between 40-220 torr with constant temperature and vapor pressure of hydrocarbon (20 torr). The results were plotted in Fig. 5, which showed an increase in the activity of hydrogenation with the partial pressure of hydrogen and reached a maximum around 160 torr, then declined with the increase of hydrogen partial pressure. The mechanism of Langmuir-Hinshelwood of competitive adsorption on the surface of catalyst could be the origin of this behaviour, where the hydrogen atoms occupied the most of the available sites on the surface at higher pressures. Similar phenomenon has been explained by Frennet *et al.* (1978), in their proposed kinetic

model, the reaction rate equation includes two terms; one depending on the hydrogen $f(\theta_H^0, P_H)$, the other one being function of the hydrocarbon coverage $g(\theta_c)$. At high hydrogen pressure and low θ_c , an inhibition term, $(1-\theta_H^0)^2$, contributes to the negative order with respect to hydrogen.

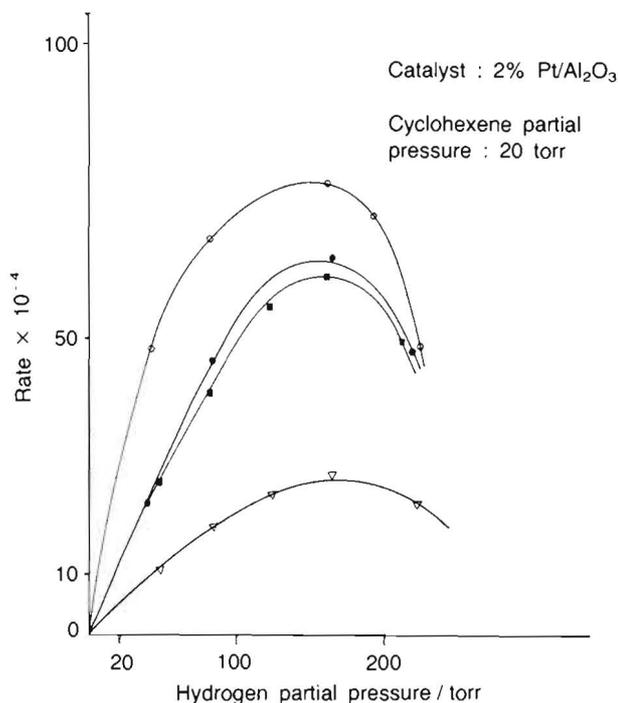


Fig. 5. Effect of the partial pressure of hydrogen on the rate of hydrogenation (torr min^{-1} , g-Pt^{-1}), ∇ 303; \bullet 323K; \circ 348K; \blacksquare 373K

On the other hand, Fig. 6 shows variation of activity with temperature at different pressures of hydrogen. We noticed, a maximum in the rate of hydrogenation at about 350 K, which cannot be caused by catalysts poisoning since hydrogen was introduced before each run for ten minutes at the reaction temperature, then pumped out, in order to minimize variation in catalytic activity. Figure 7 shows that, the activity remains constant with the number of runs. Moreover, a diffusion limitation could be the cause of this maximum, but the small particle size of catalyst used and the low conversion obtained at initial rate may eliminate this effect. The decrease in the rate of hydrogenation was also observed by Franco *et al.* (1980), and they suggested, that an insufficient amount of adsorbed hydrogen could be the cause of the reaction rate decrease at higher temperatures.

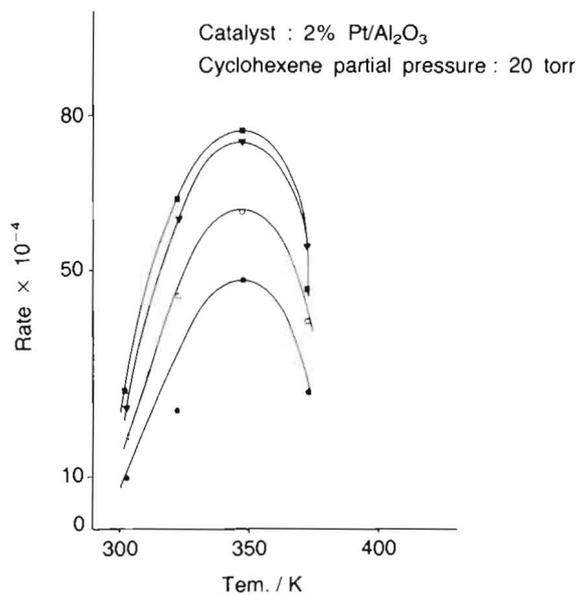


Fig. 6. Effect of the temperature on the rate of hydrogenation (torr min⁻¹, g-Pt⁻¹), ● P_{H₂} = 40 torr; ○ P_{H₂} = 80 torr; ▼ P_{H₂} = 120 torr; ■ P_{H₂} = 160 torr

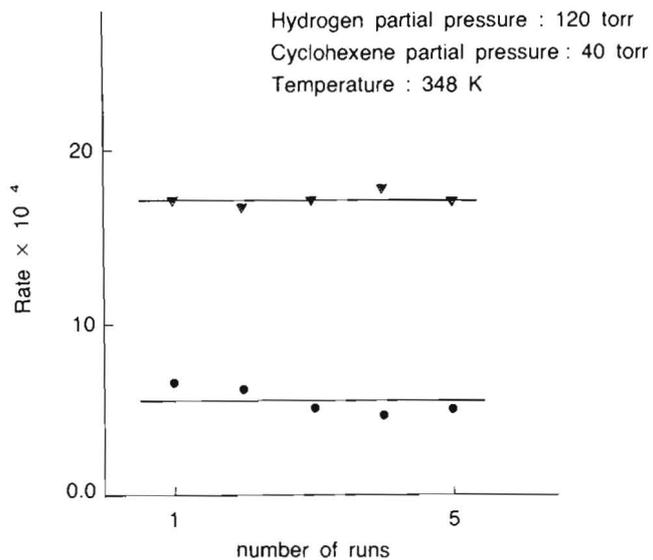


Fig. 7. Effect of the number of runs on the rate of hydrogenation (torr min⁻¹, g-Pt⁻¹), ▼ 0.2% Pt/Al₂O₃; ● 2% Pt/Al₂O₃

The order of reaction with respect to cyclohexene was determined at different temperatures, the partial pressure of hydrogen was kept constant at 120 torr, and the partial pressure of cyclohexene was varied from 20-80 torr; the order has been found to be negative (-0.30) at 303 K and changed from about 0.4 to 0.64 at higher temperatures.

Values of the reaction order with respect to hydrogen at different temperatures and hydrogen pressures are listed in Table 1.

Table 1. Values of the reaction order with respect to hydrogen at different hydrogen pressures and temperatures

temp. K	Hydrogen Pressure Range (torr)		
	40 - 125	125 - 160	160 - 230
303	0.86 a)	0.45 b)	-0.78 c)
323	0.74	0.49	-1.2
348	0.5	0.2	-1.2
a) ± 0.063 , b) ± 0.02 , c) ± 0.12			

However, the order of reaction with respect to hydrocarbon and to hydrogen depends upon both temperature and pressure of hydrocarbon and hydrogen, respectively.

The rates of hydrogenation using different catalysts were measured at series of temperature between 303-348 K, and at standard value of hydrogen partial pressure (120 torr) and cyclohexene partial pressure of (40 torr). The data for the three catalyst are shown in the Arrhenius plots in Fig. 8; from the slopes of these plots the apparent activation energies of the cyclohexene hydrogenation were determined and are given in Table 2.

The values of activation energies are in accordance with those obtained for such reaction, (Tinzmann 1981 and Segal 1978). The experimental data, represented in Fig. 9, show that the hydrogenation of cyclohexene seems to be a structure-insensitive reaction, as it has been mentioned by several authors (Segal *et al.* 1978, and Cinneide and Clarke 1973), with the exception of the data at high temperature, where the activities exhibited a variation with dispersion of platinum. These variations might be due to the presence of oxygen which appeared to behave as an activator at high temperature, (Cinneide and Clarke 1973), or to changes in the level of residual chlorine arising from chloroplatinic acid in catalyst preparation.

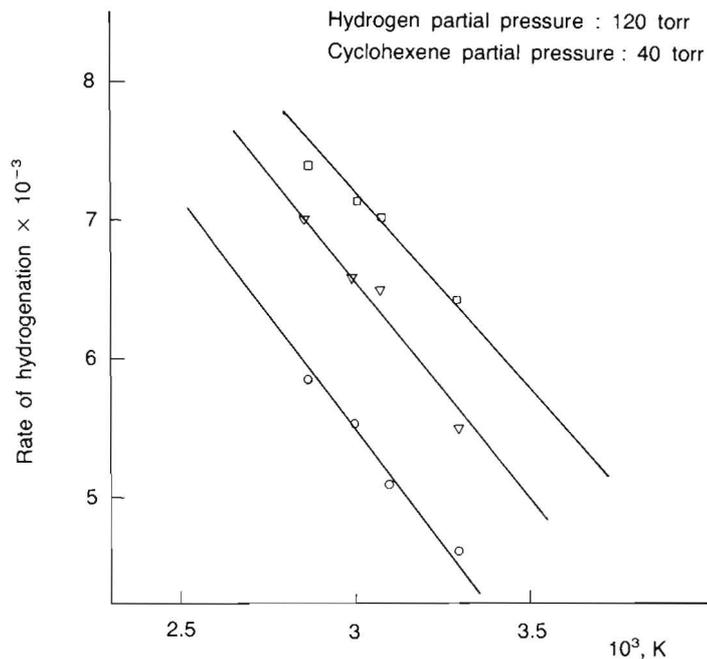


Fig. 8. The reaction rate of hydrogenation ($\text{torr min}^{-1} \text{g-cat}^{-1}$) as a function of temperature (K), \circ 0.2% Pt/Al₂O₃; ∇ 1% Pt/Al₂O₃; \square 2% Pt/Al₂O₃

Table 2. Kinetic parameters of cyclohexene hydrogenation on Pt/Al₂O₃ catalysts

Pt wt %	a) Rate of hydrogenation activity	b) D %	c) Reaction order m	d) n	e) Apparent Activation Energy E _a Kj. mole ⁻¹
0.2	4.80×10^4	(96)	(e) 0.7	(f) -0.05	(g) 27.685
1	2.51×10^4	(82)	1	-0.26	25.981
2	3.17×10^4	(75)	0.8	-0.3	23.279

a) $P_c = 40$ torr, $P_h = 120$ torr
Reaction temperature = 303 K

b) Dispersion (percentage exposed)

c) Rate = $k P_h^m P_c^n$
Reaction temperature for 0.2% = 348 K

d) Temperature range = 303-348 K

e) ± 2.5 Kj. mole⁻¹

f) ± 0.01 , g) ± 0.06

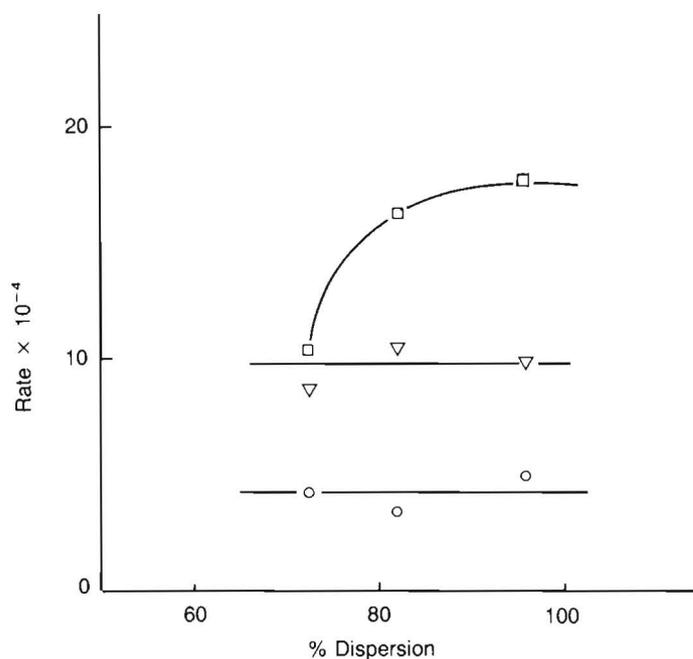
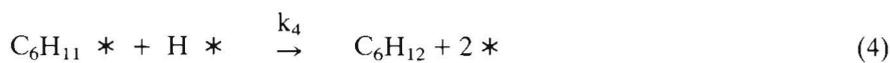
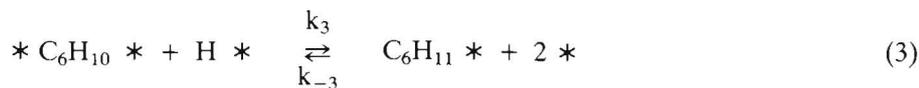
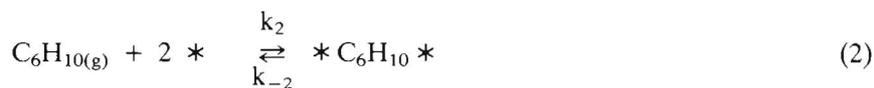


Fig. 9. Effect of dispersion on the rate of hydrogenation (torr min⁻¹ per Pt atom surface) at different temperature, ○ 303K; ▽ 323K; □ 348K

The results obtained in this work permit us to suggest that, the hydrogenation mechanism proceeds *via* associative mechanism initially proposed by Horiuti and Polanyi (1934).



The equilibria (1) and (2) are established rapidly, steps (3) and (4) indicate the removal of adsorbed reactants, the latter is considered an irreversible process with rate constant k_4 . During their studies on the hydrogenation of cyclohexene on ZrO_2 -supported Pd, Yong Lee *et al.* (1981) showed that the rate determining step is the addition of a hydrogen atom to the cyclohexyl species.

The rate of reaction then could be written as:

Rate = $k_4\theta_a\theta_h$ (5), where θ_a is the surface concentration of the monoadsorbed intermediate (cyclohexyl).

The surface coverages of cyclohexane and hydrogen may be obtained from the appropriate Langmuir equations:

$$\theta_h = \frac{K_h^{\frac{1}{2}}P_h^{\frac{1}{2}}}{1 + K_eP_e + K_h^{\frac{1}{2}}P_h^{\frac{1}{2}}} \quad (6), \quad \theta_e = \frac{K_eP_e}{1 + K_eP_e + K_h^{\frac{1}{2}}P_h^{\frac{1}{2}}} \quad (7)$$

Considering the conditions, where cyclohexene is strongly adsorbed and hydrogen weakly adsorbed, the surface coverages relationship simplifies to:

$$\theta_h \propto P_h^{\frac{1}{2}} \quad (8) \quad \text{and} \quad \theta_e \sim 1 \quad (9)$$

and θ_a can be calculated using the steady state approximation on the production and consumption of adsorbed cyclohexyl species. $k_3\theta_e\theta_h = k_{-3}\theta_a + k_4\theta_a\theta_h$ (10), from equations (5), (8), (9) and (10) the rate is given by:

$$R = \frac{k_3k_4(K_h^{\frac{1}{2}}P_h^{\frac{1}{2}})^2}{(k_{-3} + k_4K_h^{\frac{1}{2}}P_h^{\frac{1}{2}})} \quad (11)$$

Now, at low pressure, we have

$$k_{-3} \gg k_4K_h^{\frac{1}{2}}P_h^{\frac{1}{2}} \quad \text{and} \quad R = \frac{k_3k_4}{k_{-3}} K_hP_h \quad (12)$$

and the rate will be proportional to the hydrogen pressure. At high pressure, $k_{-3} \ll k_4K_h^{\frac{1}{2}}P_h^{\frac{1}{2}}$ and $R = k_3K_h^{\frac{1}{2}}P_h^{\frac{1}{2}}$ (13), and the rate will vary as the square-root of the hydrogen pressure. At higher pressure of hydrogen, the rate expression may be written as: (14)

$$R = \frac{k_3k_4K_eK_hP_eP_h}{(1 + K_eP_e + K_h^{\frac{1}{2}}P_h^{\frac{1}{2}})^2 [k_{-3} (1 + K_eP_e + K_h^{\frac{1}{2}}P_h^{\frac{1}{2}}) + k_4K_h^{\frac{1}{2}}P_h^{\frac{1}{2}}]}$$

which is rewritten in an approximate form.

$$R = \frac{k_3 k_4 K_e P_e}{(k_{-3} + k_4) K_h^{\frac{1}{2}} P_h^{\frac{1}{2}}} \quad (15),$$
 this indicates that, the rate at higher pressure of hydrogen is inversely proportional to $P_h^{\frac{1}{2}}$. Figure 10 shows good linear plots of the observed values of the rate versus P_h , $P_h^{\frac{1}{2}}$ and $P_h^{-\frac{1}{2}}$, which verifies the validity of equations (12), (13) and (15), and therefore the mechanism proposed.

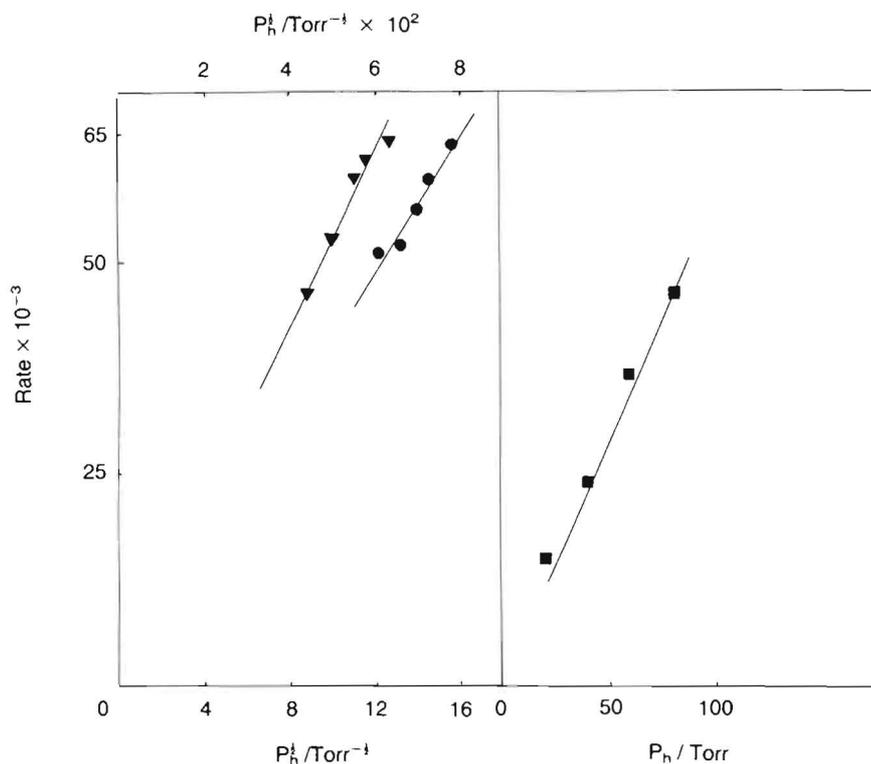


Fig. 10. Plots of rate of hydrogenation ($\text{torr min}^{-1}\text{g-Pt}^{-1}$) versus, ■ P_h , ▼ $\sqrt{P_h}$ and • $1/\sqrt{P_h}$.

References

- Cinneide, A.D.O. and Clarke, J.K.A. (1973) Catalysis on supported Metals, *Catalysis Rev.* 7: 213.
 Davies, S.M., Zaera, F. and Somorjai, G.A. (1982) The reactivity and composition of strongly adsorbed carbonaceous deposits on platinum model of the working hydrocarbon conversion catalyst, *J. Catalysis* 77: 439-459.
 Dixon, G.M. and Singh, K. (1969) Catalysis over coprecipitated nickel-alumina effect of nickel content on the hydrogenation of benzene, *Trans. Faraday Soc.* 65: 1128-1137.

- Franco, H.A. and Phillips, M.J.** (1980) Gas phase hydrogenation of benzene on supported nickel catalyst, *J. Catalysis* **63**: 346-354.
- Frennet, A., Lienard, G., Grucq, A. and Deglols, L.** (1978) effect of Multiple sites and competition in adsorption on the Kinetics of reactions catalysed by metals, *J. catalysis* **53**: 150-163.
- Horiuti, I. and Polanyi, M.** (1934) Exchange reaction of hydrogen on metallic catalysts, *Faraday Soc.* **30**: 1164-1170.
- McConica, Carol Mclellan,** (1982) *The hydrogenation of cyclohexene by supported nickel catalysts*, Ph.D. Thesis, Stanford University.
- Pines, H., Oberg, R. and Ipatieff, V.N.** (1948) Catalytic dehydrogenation of Pinane and P-Menthane studies in the terpene series. VIII. Effect of catalyst, solvent and temperature on the dehydrogenation of pinane and P-Menthane, *J. Amer. Chem. Soc.* **70**: 533-537.
- Rizk, Samir S.** (1975) *Surface and catalytic studied on supported copper-alumina catalysts*, M.Sc. Thesis, Ain Shams University, Cairo.
- Segal, E., Madon, R.J. and Boudart, M.** (1978) Catalytic hydrogenation of cyclohexene vapor-phase reaction on supported platinum, *J. Catalysis* **52**: 45-49.
- Sousi, G.N.** (1985) *Heterogeneous catalysts (Pt/Al₂O₃ - Pt/TiO₂), preparation, surface and catalytic studies*, M.Sc. Thesis, King Saud Univ., Riyadh.
- Spendel, L. and Boudart, M.** (1960) Dispersion of platinum on supported catalysts, *J. Phys. Chem.* **64**: 204-207.
- Tauqi Khan, M.M., Mehreen, A. and Swamy, B.** (1981) Homogeneous hydrogenation of cyclohexene and 1-heptene catalyzed by binuclear complexes of rhodium (I) iridium (I), *Indian J. Chem.* **20A**: 359-362.
- Tauqi Khan, M.M., Rafeeq, M., Vancheesan, S. and Swamy, B.** (1981) Homogeneous hydrogenation of cyclohexene catalysed by ruthenium (II) complexes, *Indian Journal Chem.* **20A**: 564-566.
- Tinzmann, M.** (1981) Catalyseur de Ziegler insoluble a base de Ni (II) et de Al(C₂H₅)Cl pour l'hydrogenation du cyclohexene: elaboration et comportement, *Bull. de la Societe Chimique de France* No 5-6: 1-193-197.
- Yong Lee, Yasunobu Inoue and Iwao Yaswori** (1981) Catalytic activity of highly dispersed palladium. I. The mechanism of cyclohexene hydrogenation and the role of ZrO₂ support, *Bull. Chem. Soc. Japan* **54**: 13-19.

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حركية تفاعل هدرجة الهكسين الحلقي الغازي باستعمال وسائط من البلاطين المحمول على الألومينا في النظام الثابت

عرفان زهراء و سليمان الخويطر و عصام عمار

قسم الكيمياء - جامعة الملك سعود - ص. ب ٢٤٥٥ الرياض ١١٤٥١
المملكة العربية السعودية

تمت دراسة حركية هدرجة الهكسين الحلقي على وسائط البلاطين المحمول على الألومينا في النظام الثابت، بين درجتي حرارة ٣٠٣ و ٣٧٣ كلفن، وعند ضغوط جزئية للهيدروجين والهكسين الحلقي بين ٤٠ - ٢٢٠ ملمتر زئبق و ٢٠ - ٨٠ ملمتر زئبق على التوالي.

ولقد حسبت رتبة التفاعل بالنسبة للهيدروكربون، ووجد أن قيمتها سالبة عند درجة الحرارة المنخفضة، وتساوي ٠,٥ تقريباً عند درجات الحرارة العالية. أما بالنسبة للهيدروجين فإنها تأخذ قيماً تتراوح ما بين ٠,٨ و ١ - بزيادة الضغط. إن النتائج التجريبية لهذا البحث تبرهن على أن تفاعل الهدرجة يتم وفق الآلية المشاركة.