

The effect of Pretreatment Conditions on the Activity and Selectivity of Pt/Al₂O₃ Catalyst

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ABSTRACT. The kinetics of heterogeneous catalytic conversion of cyclohexane (1) and cyclohexene (2) were studied over Pt/Al₂O₃ catalyst (A), using a flow technique under normal pressure. The industrially prepared catalyst was pretreated by air (AI) and/or with hydrogen (AII) at 500° C.

The catalytic activity was measured in the temperature range 360-430° C for (1) and 160-260° C for (2) at space velocity $13.70-33.39 \times 10^{-2}$ and 13.17 to 32.10×10^{-2} min⁻¹ for (1) and (2), respectively. The gaseous and liquid products of the conversion reaction were analysed using chromatography. The kinetics of gaseous and liquid products revealed a zero order reaction in all cases with (1) and (2), respectively. The apparent activation energy was calculated to be 10.1 and 10.6 kcal mol⁻¹ for (1) and (2) independent of space velocity.

The selectivity and activity of the catalyst vary with the pretreatment conditions and experimental temperature. The gain in the mass of the catalyst after participation in conversion and the formation of products is not a stoichiometric process in case of (AI) and (AII) catalyst are explained by polymolecular mechanism.

The study of heterogeneous catalytic processes using a flow technique is one of the important aspects of industry from a theoretical and practical point of view. The widespread use of platinum/alumina as a catalyst stimulated investigator to study the nature of catalyst and the details of the mechanism of catalytic processes. However, despite intensive investigations of this subject, there is no general agreement on the nature of the dehydrogenation and disproportionation processes even on one and the same catalyst (Balandin 1969, Krylov 1970, Karpinski and Koscielski (1980) and Ezzo *et al.* 1983) In the present investigation, an attempt is made to study the effect of pretreatment conditions of platinum/alumina catalyst on its activity and selectivity in heterogeneous catalytic conversion of cyclohexane and cyclohexene using a flow technique under normal pressure.

Experimental

Material

An industrially prepared platinum/alumina catalyst was RD150 0.6% Pt on γ -alumina. Sinclair-Baker, Engelhard Industries Company, U.S.A.

The cyclohexane and cyclohexene were prepared as reported by Ezzo *et al.* (1981), and they were chromatographically pure.

Apparatus and Techniques

The catalytic activity was measured using a flow technique. The reactant was introduced by a microdose pump (Unipan 335A) and the speed of feeding was varied in the range $(13.70\text{--}33.39) \times 10^{-2} \text{ min}^{-1}$. The reaction temperature was in the range 160–430° C. The catalyst sample (of volume 1 ml) was introduced into a silica tube reactor with an internal diameter of 12 mm. The reactor was heated by a tubular electric furnace, the temperature of which was controlled to $\pm 0.1^\circ \text{C}$. The reactor and the furnace were mounted in an inclined position.

The gaseous and liquid products were analysed in a programmed gas-liquid chromatograph with a heated dual flame ionization detector (Pye series 104) and 2/10 PEGA using nitrogen as the carrier gas.

Activation of the Catalyst Sample

Each catalyst sample was activated *in situ* by calcination at 500° C for 4 hr in a current of dry air free from CO_2 (catalyst AI) or in a current of dry hydrogen free from H_2O (catalyst AII). The activated catalyst was then cooled from the activation temperature to the catalytic reaction temperature. The activation temperature was chosen to be 500° C as required from its specification.

Results and Discussion

Effect of the Space Velocity of Cyclohexane and /or Cyclohexene on its Catalytic Conversion

The results obtained from the experiments done without using a catalyst showed that the silica glass of the catalytic apparatus, catalytic reactor, and the glass wool had no catalytic activity on the conversion of cyclohexane and cyclohexene under the experimental conditions.

The reaction temperature was maintained and cyclohexane and/or cyclohexene was allowed to pass over $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst A at various space velocities. This experiment was repeated at different temperatures specific for cyclohexane and cyclohexene.

The kinetics of cyclohexane and/or cyclohexene conversion was studied by using 1 ml of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst (A) pretreated with dry air (AI) and/or with hydrogen (AII) at 500°C at space velocity from 13.70 to 33.39×10^{-2} and 13.17 to $32.10 \times 10^{-2} \text{ min}^{-1}$ and temperature ranged from 360 to 430 and 160 to 260°C for cyclohexane and cyclohexene, respectively.

The gaseous products were methane and hydrogen in both cases. The volume of gaseous products was determined at various intervals. When this volume is plotted against time a straight line is obtained, the slope of which gave the rate of formation of the gaseous products, which was then calculated at STP (V° in millilitres per minute).

Figures 1 and 2 (a) and (b) represent the effect of variation of time of contact τ on the rate of conversion of cyclohexane and cyclohexene on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst (A) (a – for AI and b – for AII). The curve designated by (1) in these figures represents the effect of variation of time of contact on the formation of gaseous products. Whereas curves 2, 3 and 4 show the variation of the % formation of benzene (as calculated from chromatographic analysis), % cyclohexane conversion Fig. 1 and % cyclohexane formation Fig. 2, and % conversion of cyclohexene, respectively, with time of contact τ at 380°C for cyclohexane 220°C for cyclohexene.

The corresponding data for the dependence of the rate of catalytic dehydrogenation of cyclohexane and catalytic disproportionation of cyclohexene over $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst (A) on time of contact are given in Tables 1 and 2.

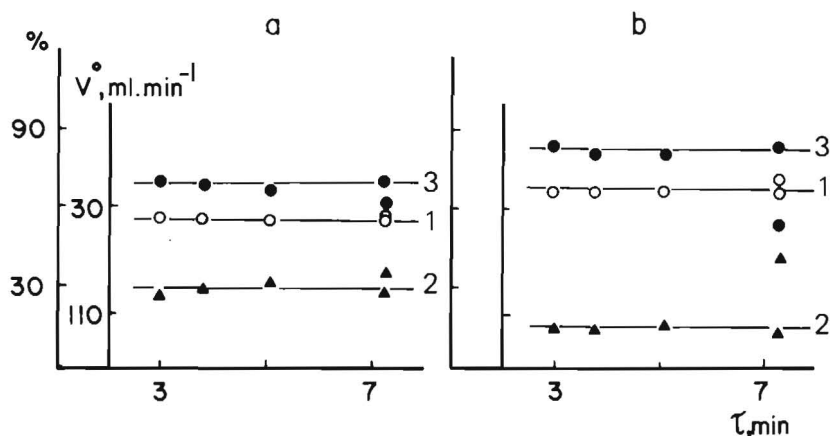


Fig. 1. The effect of variation of time of contact on the conversion of cyclohexane on $\text{Pt}/\text{Al}_2\text{O}_3$ A catalyst at 380°C .

a – AI b – AII
(1- V° ; 2-%-benzene; and 3-% cyclohexane)

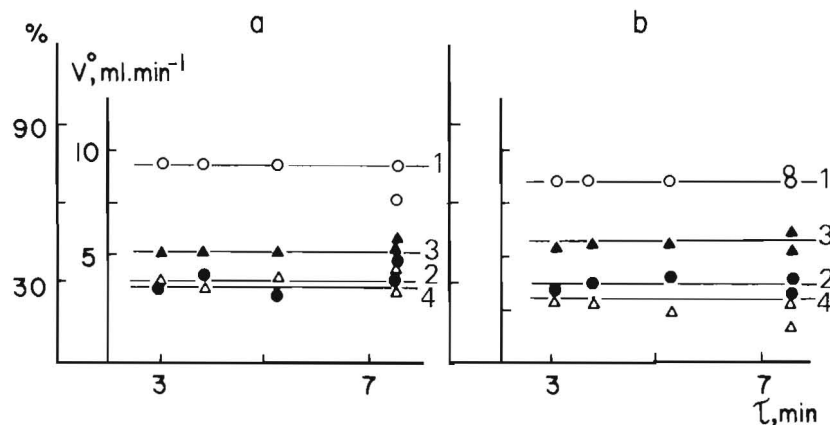


Fig. 2. The effect of variation of time of contact on the conversion of cyclohexene on Pt/Al₂O₃ A catalyst at 220°C.

a - AI b - AII

(1-V°; 2-% benzene; 3-% cyclohexane; and 4-% cyclohexene)

It can be seen from Fig. 1 and 2 and Tables 1 and 2 that the rate of formation of gaseous products, % formation of benzene, % conversion and formation of cyclohexane, and % conversion of cyclohexene are independent of the rate of flow, *i.e.* the reaction of conversion of cyclohexane and cyclohexene is a zero order reaction. This indicates that the catalytic reaction conforms to a Langmuir-Hinshelwood mechanism as reported by Kiperman (1964). The catalyst surface, or at least the active part of it, is saturated with chemisorbed cyclohexane and/or cyclohexene molecules.

It follows from the analysis of the liquid products, given in Table 1, that cyclohexane is dehydrogenated to benzene, over Pt/Al₂O₃ catalyst AI and AII. However, the analysis of liquid products given in Table 2 shows that cyclohexene is disproportionated to cyclohexane and benzene over Pt/Al₂O₃ catalyst AI and AII. The percent formation of benzene and cyclohexane depends on the nature of the catalyst and the experimental temperature.







The mass of the catalyst is found to increase after its use in cyclohexane and cyclohexene conversion. The apparent gain in weight of the catalyst, after the course of rate determination, is given in Tables 1 and 2. It can be seen from these results that the apparent gain in weight of catalyst AI has an affinity to decrease with temperature in the case of cyclohexane and cyclohexene, respectively. However, on AII, catalyst can be taken as constant value and has an affinity to increase with temperature for cyclohexane and cyclohexene conversion, respectively.

Table 1. The effect of catalyst pretreatment on the catalytic conversion of cyclohexane on Pt/Al₂O₃ catalyst in flow system.

Temp. °C	F X10 ⁻² , min ⁻¹	V° ml min ⁻¹		E kcal. mol ⁻¹	Weight Gain %		Analysis of the liquid products			
							AI		AII	
		AI	AII				AI & AII	AI	AII	
360	13.70	19.9	28.5	10.1	4.80	1.20	10.70	89.30	35.90	64.10
	19.69	19.9	28.5	10.1	4.80	1.20	10.10	89.90	35.20	64.80
	26.55	19.9	28.5	10.1	4.80	1.20	12.10	87.90	36.20	63.80
	33.39	19.9	28.5	10.1	4.80	1.20	13.30	86.70	37.90	62.10
	13.70	19.2	28.5	10.1	4.80	1.20	7.50	92.50	34.73	65.27
380	13.70	28.8	36.5	10.1	1.60	1.60	36.94	63.66	44.50	55.50
	19.69	28.1	34.2	10.1	1.60	1.60	31.80	68.20	17.60	82.40
	26.55	28.1	34.2	10.1	1.60	1.60	29.70	70.30	17.60	82.40
	33.39	28.1	34.2	10.1	1.60	1.60	28.20	71.80	14.90	85.10
	13.70	28.1	34.2	10.1	1.60	1.60	29.10	70.90	13.89	86.11
400	13.70	33.5	38.7	10.1	2.20	—	61.30	38.70	54.70	45.30
	19.69	31.6	38.7	10.1	2.20	—	42.60	57.40	54.70	45.60
	26.55	31.6	38.7	10.1	2.20	—	40.00	60.00	51.10	48.90
	33.39	31.6	38.7	10.1	2.20	—	35.60	64.40	53.30	46.70
	13.70	31.6	38.7	10.1	2.20	—	42.60	57.40	51.10	48.90
430	13.70	44.3	47.1	10.1	—	—	42.70	57.30	38.20	61.80
	19.69	44.3	13.7	10.1	—	—	29.91	70.09	11.90	88.10
	26.55	44.3	13.7	10.1	—	—	29.06	70.94	9.30	90.70
	33.39	44.3	13.7	10.1	—	—	27.30	72.70	8.90	91.10
	13.70	44.3	13.7	10.1	—	—	31.90	68.10	8.30	91.70

It follows from Table 1 that, at 360 and 400° C, the catalyst AII is more active than AI in the dehydrogenation of cyclohexane to benzene and in the formation of gaseous products. However, at 360° C, AI is more active in benzene formation than AII under the same conditions. Moreover, at 430° C, AI is more active than AII in dehydrogenation and decomposition processes of cyclohexane. Indeed, at 380° C, AI is more active in dehydrogenation process than AII, whereas the reverse is correct in the formation of gaseous products.

Table 2. The effect of catalyst pretreatment on the catalytic disproportionation of cyclohexene on Pt/Al₂O₃ catalyst in flow system.

Temp. °C	F 10 ⁻² min ⁻¹	V° ml min ⁻¹		E kcal mol ⁻¹ AI & AII	Weight Gain %		Analysis of liquid products, %					
		AI					AII					
		AI	AII		AI	AII						
160	13.17	8.7	1.4	10.6	27.3	2.80	41.47	32.28	26.25	23.60	2.70	73.70
	18.93	8.7	1.4	10.6	27.3	2.80	39.85	31.22	28.93	6.80	1.40	91.80
	25.51	8.7	1.4	10.6	27.3	2.80	35.71	29.85	34.44	3.76	1.88	94.36
	32.10	8.7	1.4	10.6	27.3	2.80	36.09	28.44	35.47	4.00	1.70	94.30
	13.17	8.7	1.4	10.6	27.3	2.80	34.96	31.80	33.24	5.40	2.70	91.90
220	13.17	13.3	13.1	10.6	12.0	1.80	47.00	39.30	13.70	52.00	32.00	16.00
	18.93	13.3	11.6	10.6	12.0	1.80	39.80	25.80	34.40	46.00	33.00	21.00
	25.51	13.3	11.6	10.6	12.0	1.80	40.19	32.71	27.10	45.30	30.20	24.50
	32.10	13.3	11.6	10.6	12.0	1.80	40.00	27.27	32.73	43.00	28.00	29.00
	13.17	10.0	11.6	10.6	12.0	1.80	37.30	30.27	32.43	44.10	28.30	27.60
240	13.17	19.4	2.9	10.6	5.70	12.40	45.50	50.80	3.70	12.70	2.50	84.80
	18.93	19.7	2.9	10.6	5.70	12.40	48.70	43.50	7.80	4.70	1.60	93.70
	25.51	19.7	2.9	10.6	5.70	12.40	48.80	43.40	7.80	0.80	1.60	97.60
	32.10	19.7	2.9	10.6	5.70	12.40	46.20	46.40	7.40	0.80	1.60	97.60
	13.17	19.7	2.9	10.6	5.70	12.40	48.20	45.20	6.60	3.10	3.10	93.80
260	13.17	11.9	15.5	10.6	9.20	6.30	37.20	30.80	32.00	28.80	31.40	39.80
	18.93	11.9	15.5	10.6	9.20	6.30	29.50	26.10	44.40	31.00	30.00	39.00
	25.51	11.9	15.5	10.6	9.20	6.30	30.66	25.94	43.40	30.00	27.50	42.50
	32.10	11.9	15.5	10.6	9.20	6.30	26.50	28.00	45.50	27.60	28.00	44.40
	13.17	11.9	16.2	10.6	9.20	6.30	29.58	28.17	42.25	27.50	18.60	53.90

It can be seen from Table 2 that, at 220 and 260° C, the catalyst AI and AII has the same activity, under the present experimental conditions, in the disproportionation process of cyclohexene. However, there are more condensating products formed on the surface of AI than that on AII. Moreover, at 160° C, AI is more active and more stable than AII, since the latter loses its activity after the first run. The same effect was observed at 220° C.

The results obtained, therefore, indicate that the selectivity and activity of Pt/Al₂O₃ catalyst vary with the pretreatment conditions and experimental temper-

atures. It should be noticed that the formation of benzene and cyclohexane from cyclohexene is not a stoichiometric process in case of catalyst AI and AII.

The effect of Reaction Temperature (the Determination of the Apparent Activation Energy)

The data on the rate V° of formation of gaseous products for cyclohexane and cyclohexene at different flow rates determined at various temperatures allowed us to calculate the apparent activation energy E of conversion of cyclohexane and cyclohexene Fig. 3 (a – for cyclohexane conversion on Pt/ Al_2O_3 catalyst AI and b – for cyclohexene disproportionation on catalyst AII). This energy was also determined from data on the percentage conversion of cyclohexane and cyclohexene at various temperatures. The methods gave identical values. Table 1 and 2 includes the calculated energy of activation for cyclohexane and cyclohexene in contact with Pt/ Al_2O_3 catalyst AI and AII at each space velocity and different temperatures.

It is evident from Table 1 and 2 that the apparent activation energy is almost independent of the contact time, working time of the catalyst AI and AII, and the pretreatment gas. The apparent activation energy was found to have a value of 10.1 and 10.6 kcal mol⁻¹ of the catalytic conversion of cyclohexane and cyclohexene on Pt/ Al_2O_3 catalyst AI and AII, respectively.

From the V° values given in Table 1 it can be seen that the rate of formation of gaseous products is generally increased with temperature. However, the rate of benzene formation increased with temperature until 400° C, then decreased in the case of AI catalyst. When using AII catalyst the same behaviour is noticed only in the case of the fresh portion of the catalyst. If the catalyst AII is kept for 0.5, 1 and 1.5 hr in cyclohexane vapour, different results are obtained, especially at 380° C.

It follows, from Table 2, that the rate of formation of gaseous products is generally increased with temperature until 240° C and then decreased for AI catalyst. In the case of using AII catalyst, the rate increased with temperature except at 240° C, where the rate decreased. The rate of formation of cyclohexane and benzene has different behaviours. The maximum yield of benzene was observed at 240 and 220° C during the conversion of cyclohexene over AI and AII catalyst. Moreover, the maximum yield of cyclohexane was noticed at 240° C over AI and at 220° C over AII catalyst, independent of the working time of the catalyst. It is evident, therefore, that the conversion of cyclohexene into benzene and cyclohexane is not a parallel reaction, but proceeds through an intermediate compound having different characters.

We believe that the conversion of cyclohexane and cyclohexene over Pd/ Al_2O_3 catalysts takes place through the formation of a polymolecular catalytic complex $[(\text{C}_n\text{H}_{2n})_n]_{\text{ads}}^{\text{K}}$ which can be decomposed in different ways according to the kinetic

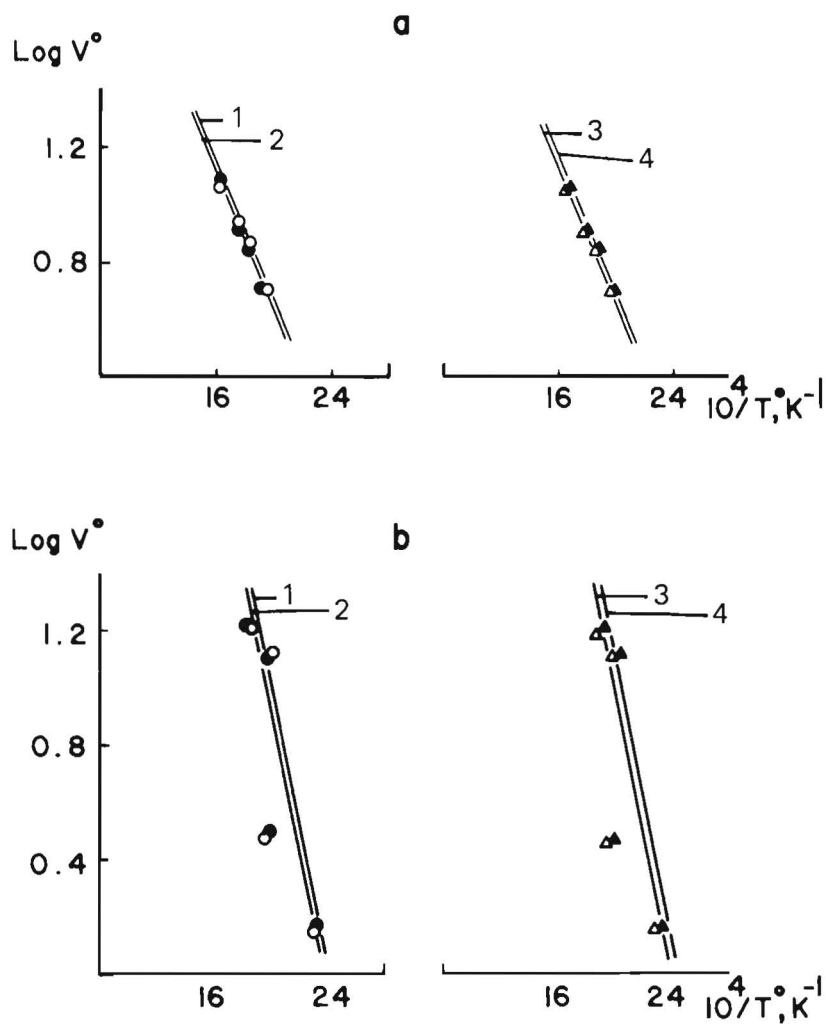


Fig. 3. The effect of temperature on the catalytic conversion of cyclohexane (a) and cyclohexene (b) on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst

a. AI at $f \times 10^{-2} \text{ min}^{-1}$ 1 – 13.70; 2 – 19.69; 3 – 26.55; and 4 – 33.39).

b. AII (at $f \times 10^{-2} \text{ min}^{-1}$ 1 – 13.17; 2 – 18.93; 3 – 25.51; and 4 – 32.10).

conditions to give various catalytic products as reported before by Ezzo and Rudenko (1979). The conversion of cyclohexane and cyclohexene over the Pt/ Al_2O_3 catalyst can also be described by a polymolecular mechanism. The polymolecularity of the process is indicated by the products obtained and by the gain in catalyst weight during the catalytic conversion of cyclohexane and cyclohexene.

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دراسة تأثير ظروف المعالجة على نشاطية واختيارية حفاز Pt/Al_2O_3

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تمت دراسة كيناتيكية التحول الحفزى غير المتجانس للهكسان
الحلقى (١) والهكسين الحلقى (٢) على حفاز $(A)Pt/Al_2O_3$
بواسطة جهاز التيار المتدفق تحت الضغط العادى . وعولج الحفاز
المحضر صناعيا بواسطة الهواء (AI) أو الهيدروجين (AII) عند
٥٠٠ م° .

قيست نشاطية الحفاز مع الهكسان الحلقى فى مدى حرارى
٣٦٠-٤٣٠ م° ومع الهكسين الحلقى فى مدى حرارى
١٦٠-٢٦٠ م° عند سرعة فراغية مقدارها ٧، ١٣-٣٩، ٣٣ ×
١٠-٢ فى حالة الهكسان الحلقى و ١٧، ١٣ إلى ١، ٣٢ × ١٠-٢
دقيقة^{-١} فى حالة الهكسين الحلقى .

تم تحليل نواتج تفاعل التحول السائلة والغازية باستخدام
الكروماتوجراف . أوضحت كيناتيكية ظهور نواتج التحول
السائلة والغازية أن التفاعل ذا رتبة صفرية فى الحالتين .

وجد أن قيمة طاقة التنشيط الظاهرية للهكسان الحلقى
١، ١٠ وللهمكسين الحلقى ٦، ١٠ ك سعر/مول، وهولا يعتمد
على السرعة الفراغية .

وتتغير اختيارية ونشاطية الحفاز تبعاً لظروف معالجته ودرجة
حرارة التجربة . والزيادة فى وزن الحفاز بعد اشتراكه فى عملية
التحول وتكوين النواتج ليست عملية جزئية فى حالة الحفازين
ولكنها تفسر بميكانيكية متعدد الجزيئات .