

Ensembling and Monolayer Parameters for the Dehydrogenation of Cyclohexane over Pt/Al₂O₃ Catalyst

V. KRISHNASAMY* AND K. BALASUBRAMANIAN†

*Department of Chemical Engineering, A. C. College of Technology, Anna University, Madras 600 025, India and †Applied Science Division, MIT, Anna University, Madras 600 044, India

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The ensembling and the monolayer parameters, such as the number of atoms in an active center (n), the absolute efficiency of an active center (r_n), the number of migration regions (Z_0), average area of migration regions (Δ), fractional surface coverage (θ_c), and the average number of atoms in a region (ν), were evaluated for the dehydrogenation of cyclohexane over Pt/Al₂O₃ catalyst in vapor phase. The reaction was studied using alumina of two types in the temperature range 225–350°C at two contact times. Monoatomic ensemble is the active center in the system studied. Dependence of probability of formation of atomic ensemble (P_n) on the average number of atoms in a migration region is also given. © 1984 Academic Press, Inc.

INTRODUCTION

Reforming of naphthenes and paraffins to aromatics has been studied extensively using supported metal catalysts. Among these, platinum–alumina finds wide application for reactions (1) involving dehydrogenation, isomerization dehydrocyclization, and hydrocracking. Though various aspects relating to the above reactions, viz., the effect of support, platinum loading, mechanism, kinetics, etc. (2–6) have been studied, parameters pertaining to the theory of active ensemble have not been given due attention. In the present investigation, an attempt has been made to evaluate the ensemble (7–10) and monolayer parameters for the dehydrogenation of cyclohexane over platinum–alumina.

EXPERIMENTAL

The purity of the cyclohexane (BDH, AR) was found to be more than 99% by gas chromatographic analysis.

Two samples of alumina, one prepared from aluminum isopropoxide according to the method described by Pines and Haag

(11) and the other a commercial grade from Sarabhai-Merck, were used.

Platinum–alumina catalysts were obtained by adding calculated volumes of chloroplatinic acid in water to nine weighed samples of alumina (from aluminum isopropoxide) to give, respectively, 0.1, 0.3, 0.6, 0.9, 1.0, 1.4, 2.0, 3.0, and 4.7% platinum by weight. These samples were designated as catalysts-A. Similarly chloroplatinic acid was added to five weighed samples of commercial alumina to give, respectively, 0.2, 0.6, 1.0, 2.0, and 3.0% platinum by weight, which were designated as catalysts-B.

The slurry of each case was stirred for 3 hr and dried in a furnace at 120°C for 24 hr. Then the temperature of the furnace was raised slowly to 500°C while passing pure dry hydrogen and kept at this temperature for 8 hr. The material thus activated was powdered and sieved to 180–200 mesh particle size.

Surface Area Measurements

(i) *Support*. The surface area measurements for support were made according to BET method (12) by the adsorption of ni-

TABLE 1
 Δ , θ_c , and ν Values for the Conversion of Cyclohexane over Pt/Al₂O₃

%Pt	$(NDA)_{cat}$ (m ² /g)	$(NDA)_{cat, occupied}$ (m ² /g)	$\theta_c \times 10^3$	Cat. A, Contact time = 0.79 hr			
				ν			
				Temp. (°C)	250	300	350
				Δ	8.93×10^{-18}	10.39×10^{-18}	11.29×10^{-18}
1.4	3.80	0.76	4.17		2.12	2.47	2.69
				Cat. A, Contact time = 0.123 hr			
				ν			
				Temp. (°C)	225	250	
				Δ	2.7×10^{-18}	2.79×10^{-18}	
2.0	4.26	0.86	4.72		0.92	0.95	
3.0	4.57	0.92	5.05		1.38	1.42	
4.7	5.11	1.02	5.60		2.16	2.22	
				Cat. B, Contact time = 0.123 hr			
				ν			
				Temp. (°C)	225	250	
				Δ	1.31×10^{-18}	1.51×10^{-18}	
1.0	2.62	0.53	6.56		0.51	0.58	
2.0	3.88	0.76	9.50		1.01	1.16	
3.0	5.70	1.13	14.00		1.49	1.72	

trogen at liquid-nitrogen temperature. The values for isopropoxide alumina and commercial alumina are 181 and 80 m² g⁻¹, respectively.

(ii) *Platinum surface area.* Hydrogen adsorption was done using the same constant-volume adsorption system used in the surface area (BET) determination. The measurements were done at 250°C following a procedure similar to the one by Spindel and Boudart (13). About 5 g of the catalyst was attached to the system and evacuated to 10⁻⁵ cm Hg. The evacuated catalyst was then reduced in pure, dry flowing hydrogen at 250°C for 2 hr. The reduced catalyst was further evacuated at 450°C to an ultimate pressure of 10⁻⁶ cm Hg. The hydrogen chemisorption studies were carried out over this cleaned catalyst at 250°C. V_m values were calculated by the point B method (14) from plots of amount of hydrogen adsorbed versus equilibrium pressure.

From the amount of hydrogen chemisorbed the H/Pt ratios were calculated. The H/Pt ratio was then multiplied by $(6.02 \times 10^{23}) / (195.09 \times 1.12 \times 10^{15} \times 10^4)$ to obtain the surface areas of platinum in square meters per gram. The exposed surface area of platinum atoms in 1 g of support, $(NDA)_{cat}$, and area of platinum atoms in contact with 1 g of support, $(NDA)_{cat, occupied}$, are computed (13, 15) and the values are given in Table 1.

Apparatus and Procedure

The reactions were carried out in a fixed-bed-flow-type Pyrex glass reactor 50 cm long with 1.5 cm i.d., in the temperature range 225–350°C and at contact times of 0.123 hr (50 ml cyclohexane per hour over 4.8 g catalyst) and 0.79 hr (10 ml cyclohexane per hour over 6.2 g catalyst) at atmospheric pressure. Contact time was calculated on the basis of W/F ratio (W is the

TABLE 2

The Total Catalytic Activity Values for the Conversion of Cyclohexane at 225, 300, and 350°C

Cat.	C _t (hr)	Temp. (°C)	Number of platinum atoms/g support, $N \times 10^{-18}$									
			3.08	6.17	9.25	18.50	27.75	30.84	43.17	61.67	92.51	144.90
			Total catalytic activity, $A_n \times 10^{-19}$ molecules/sec g									
A	0.79	300	10.58 (49.9)	—	11.22 (53.0)	15.45 (72.9)	17.36 (82.0)	—	7.83 (36.9)	—	—	—
A	0.79	350	14.61 (69.0)	—	16.08 (75.9)	19.94 (94.2)	18.20 (85.9)	—	14.61 (69.0)	—	—	—
A	0.123	225	—	—	—	21.28 (15.6)	—	22.64 (16.6)	—	32.44 (23.8)	30.28 (22.2)	22.37 (16.4)
B	0.123	225	—	10.03 (7.3)	—	12.60 (9.2)	—	12.88 (9.4)	—	16.13 (11.8)	16.67 (12.3)	—

Note. The figures given in parentheses are the percentage conversion of cyclohexane.

weight of the catalyst and F is the weight rate of the reactant per hour). Pyrex glass beads (4 mm diameter) were placed above the catalyst bed to a height of 5 cm. The reactor tube was inserted into a cylindrical furnace and heated electrically to the requisite temperature. Using thermocouples the temperatures were monitored along the length of the catalyst bed and the temperature required for a particular run was maintained constant.

Prior to each run the catalyst was reduced *in situ* with hydrogen at 500°C for 3 hr. The reactant liquid was fed into the reactor by a constant feed infusion pump that could be operated for different feed rates. The liquid products collected for the first 15 min of each run (which normally covers 1 hr) were discarded. The products were analyzed using AIMIL gas chromatograph consisting of 1-m column of carbowax on Chromosorb. The products identified were benzene and hydrogen which indicates that the Pt/Al₂O₃ is selective for the dehydrogenation process. The conversion of cyclohexane varies depending on temperature, contact time, and platinum loading. The percentage conversion under various conditions are given in Table 2 in brackets. Stability of the catalyst under our reaction conditions without addition of hydrogen to the feed (16) was verified by repeating the run at 300°C, at a contact time 0.79 hr after the

use of catalyst for 15 hr. Constancy in the percentage conversion of cyclohexane assures the stability of the catalyst.

The stability along the run was verified by collecting the catalysate for every 5 min and analyzing the product. The percentage conversion is plotted against average time of cuts. The constancy of conversion after the first 15 min justifies the procedure adopted in this study.

The existence of carbonaceous deposit on the used catalyst is established by estimating the carbon. The carbon deposit is low, varying from 0.1 to 0.7% C in the temperature range studied.

Theory of Ensembles

The theory of active centers was first proposed by Taylor (17) and later adopted by several authors like Balandin (18), Schwab and Pietsch (19), and Morris and Reyerson (20). This theory, though important describes the active center in a qualitative manner. Kobozev's theory of active ensemble (10) provides methods for the determination of the composition and properties of the active center based on experimental data for different processes over metal-supported catalyst. Kobozev proposed that the active part of the catalyst consists of a few atoms having right configuration and which are located on the surface of the support. This concept was extended to alloy catalyst

by Dowden (22), Stephan *et al.* (23), and Schaik *et al.* (24).

According to the theory of ensemble if atoms of a metal are applied to the block surface of the support the atoms getting onto definite portions of the support surface need excess energy for surmounting the geometrical barriers and for motion over the entire surface. Thus, the surface of a support is divided into closed sections from an energy point of view, in which at a given temperature nonactivated motion of the atoms of the applied metal takes place. Kobozev called these sections migration regions, denoted by Z_0 . The applied atoms arrange themselves on the surface of the support in the form of isolated aggregation or ensembles consisting of a certain number of atoms localized by the regions of migrations.

Surface area of 1 g of the support is A_s and number of catalyst atoms applied to the surface of 1 g of the support is N . Number of migration regions in 1 g of the support is Z_0 . Then average area of migration region (Δ , $\text{m}^2 \text{ region}^{-1}$) will be

$$\Delta = \frac{A_s}{Z_0}. \quad (1)$$

The concentration of a catalyst on the surface of its support is expressed through the fractional surface coverage, θ_c .

$$\theta_c = \frac{(NDA)_{\text{cat. occupied}}}{A_s}. \quad (2)$$

The average number of catalyst atoms (ν) at the given fractional coverage per migration region with the area Δ will be

$$\nu = \frac{N}{Z_0}. \quad (3)$$

The values of the parameters Δ , θ_c , and ν for the system under study are given in Table 1.

Composition of an active center for a process can be determined by making use of the law of distribution of the catalyst atoms. On the basis of equal probability of catalyst atom getting into a certain region of

migration, the probability of formation of an n -atomic ensemble in one region (P_n) can be determined by Poisson's (25) distribution.

$$P_n = \frac{1}{n!} \left(\frac{N}{Z_0}\right)^n e^{-N/Z_0}. \quad (4)$$

The number of n -atomic ensemble, Z_n , is given by

$$Z_n = Z_0 P_n \quad (5)$$

or

$$Z_n = Z_0 \frac{1}{n!} \left(\frac{N}{Z_0}\right)^n e^{-N/Z_0}. \quad (6)$$

Total catalytic activity, A_n (molecules/sec · g) is defined as the number of reactant molecules reacting per second on all the catalyst atom on the surface of 1 g of a support. Specific activity, a_n (molecules/sec atom) is defined as number of molecules reacting per second on one atom of the catalyst. The expression for A_n and a_n are

$$A_n = \sum_n r_n Z_n \quad (7)$$

$$a_n = \sum_n \frac{r_n Z_n}{N}, \quad (8)$$

where r_n is the activity of one n -atomic ensemble, i.e., the absolute efficiency of an active center.

Substituting (6) in (8):

$$a_n = r_n \frac{1}{n!} \left(\frac{N}{Z_0}\right)^{n-1} e^{-N/Z_0} \quad (9)$$

where $n = 1$, a monoatomic ensemble is the active center and the equation reduces to

$$a_1 = r_1 e^{-N/Z_0}. \quad (10)$$

It is evident from this expression that specific activity decreases exponentially with increase in the concentration of catalyst atom (21). Taking the logarithm of equation

$$\log a_1 = \log r_1 - \frac{N}{2.303 Z_0} \quad (11)$$

from the straight-line plots of $\log a_1$ vs N the value of Z_0 and r_1 can be calculated.

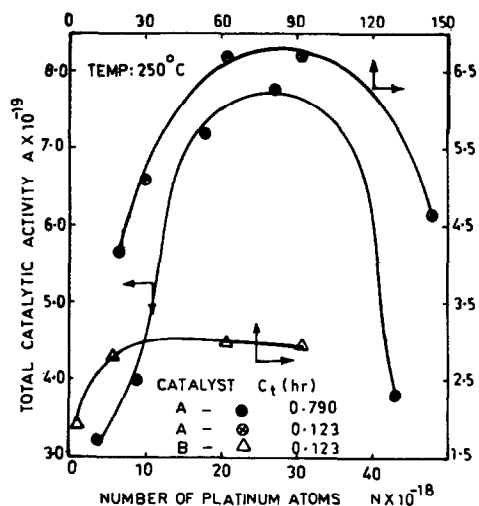


FIG. 1. Dependence of the total catalytic activity on the Pt content.

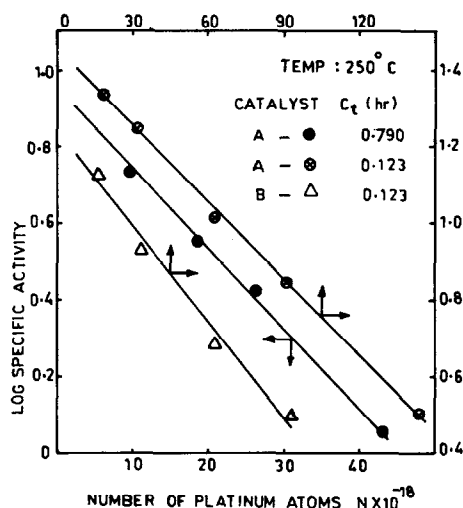


FIG. 2. Log specific activity as a function of Pt atoms.

RESULTS AND DISCUSSION

From the percentage of platinum in the two different alumina supports, the number of platinum atoms per gram of the support (N) has been calculated and given in Table 2 for the various catalysts. The total catalytic activity (A_n) for the conversion of cyclohexane is evaluated at 225, 300, and 350°C and given in the same table. A_n and $\log a_n$ values for the conversion at 250°C are plotted against N in Figs. 1 and 2, respectively. In the plots of A_n vs N , the curves

exhibit maxima (Fig. 1) whereas in the plot of a_n vs N , an exponential decrease is observed (Fig. 2) indicating the existence of monoatomic ensemble for the dehydrogenation process. The absolute efficiency and the number of migration regions for the formation of benzene are calculated using least-square regression analysis (26) and the values are given in Table 3. The governing equations for the regression analysis are given below with the correlation coefficient (CC) and standard deviation (SD) values.

TABLE 3

Composition of Active Centers Determined According to the Theory of Active Ensembles

Temp. (°C)	Contact time (C_t) (hr)	Catalyst	Active center	Absolute efficiency ^a (molecules/ensembles · sec)	Number of migration region, ^a $Z_0 \times 10^{-19}$
250	0.79	A	[Pt] ₁	9.48	2.05
300	0.79	A	[Pt] ₁	22.95	1.79
350	0.79	A	[Pt] ₁	24.43	1.64
225	0.123	A	[Pt] ₁	13.38	6.66
250	0.123	A	[Pt] ₁	28.32	6.60
225	0.123	B	[Pt] ₁	8.05	5.91
250	0.123	B	[Pt] ₁	18.22	5.03

^a By the least-square method.

Catalysts - A		$C_t = 0.79$ hr	
Temp. (°C)	Governing equation	CC	SD
250	$\text{Log } a_n = 0.977 - 2.108 \times 10^{-20} N$	0.963	0.09
300	$\text{Log } a_n = 1.361 - 2.415 \times 10^{-20} N$	0.976	0.08
350	$\text{Log } a_n = 1.387 - 2.641 \times 10^{-20} N$	0.991	0.06
Catalysts - A		$C_t = 0.123$ hr	
225	$\text{Log } a_n = 1.126 - 6.518 \times 10^{-21} N$	0.992	0.06
250	$\text{Log } a_n = 1.452 - 6.569 \times 10^{-21} N$	0.998	0.03
Catalysts - B		$C_t = 0.123$ hr	
225	$\text{Log } a_n = 0.906 - 7.355 \times 10^{-21} N$	0.974	0.06
250	$\text{Log } a_n = 1.261 - 8.618 \times 10^{-21} N$	0.981	0.07

Effect of Support ($C_t = 0.123$ hr)

The values of Δ and Z_0 are higher for catalysts - A compared to catalysts - B (Tables 1 and 3); consequently absolute efficiency values are also higher for catalysts - A. This is attributed to the higher surface area of the support.

Effect of Contact Time

The absolute efficiency value for catalysts - A is lower at 0.79 hr than at 0.123 hr. The low value at higher contact time may be due to the predominance of the reverse reaction. A separate study of the hydrogenation of benzene confirms this.

Effect of Temperature

Increase of temperature from 225 to 350°C decreases the number of migration regions. As a result of this the average area of a migration region (Table 1) and the absolute efficiency increase (Table 3).

The probability of the formation of atomic ensembles (P_n) is plotted against the average number of atoms for the formation of benzene from cyclohexane in Fig. 3. When n takes the value of unity in the Poisson's distribution equation

$$P_n = \frac{\nu^n}{n!} e^{-\nu} \quad (12)$$

maximum probability is obtained.

According to the theory of ensemble, ensemble atoms were the points of activated adsorption and chemical reaction. From the

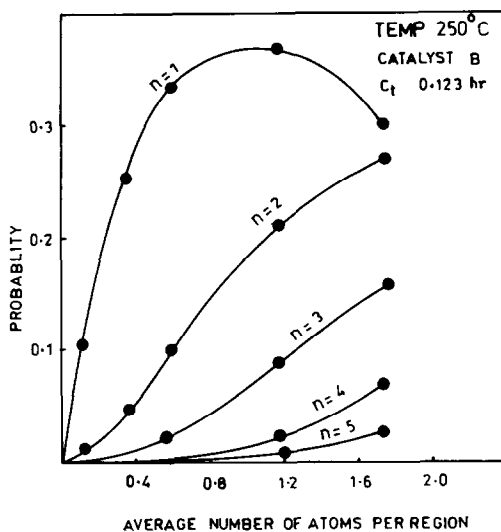


FIG. 3. Probability of formation of atomic ensembles depending on the average number of atoms per region.

experimental observation it is proved that a monoatomic ensemble is the active center in the dehydrogenation process. The dehydrogenation of cyclohexane presumes to occur almost exclusively on the metal component with single-center mechanism implying a series of π - σ shift as proposed by Ruize-Vizcaya *et al.* (27).

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