

Investigation of the mechanism of dehydrogenation of cycloalkanes over Cu/Al₂O₃ catalyst

E. M. EZZO, H. S. MAZHAR, S. A. ALI, and N. A. YOUSSEF

Department of Chemistry, Faculty of Women, Ain Shams University, Heliopolis, Cairo, Egypt

Received 16 July 1990

The heterogeneous kinetics of conversion of methylcyclohexane and cyclohexane were studied on copper/alumina catalysts, using a flow technique under normal pressure. It was found that this process is not a simple process of intermediate formation of monomolecular catalytic complex, but instead, a polymolecular catalytic one, in which the decomposition of the polymolecular complex intermediate is the rate-determining step. The textural properties and X-ray diffraction were studied for the solid samples and the nature of the intermediate, heterogeneous catalytic complex, formed was discussed.

The formation of aromatic hydrocarbons by the catalytic dehydrogenation of a saturated six-membered ring is a well known reaction. The transition metals and their oxides are active catalysts for such dehydrogenation reactions.

Dehydrogenation catalysts are, in principle, the metals of group VIII in the periodic table, copper oxides and sulfides of metals are active in hydrogenation reactions. It is known that the dehydrogenation process takes place at a temperature higher than that of hydrogenation.

The two known [1] basic modes of methylcyclohexane decomposition on dispersed metal oxide catalysts are dehydrogenation and dehydromethylation to toluene and benzene, respectively, as elementary reaction directly or indirectly *via* free radical mechanism [1, 2].

In our previous works [3—6] the heterogeneous catalytic decomposition of alcohols, alkanes, and cycloalkanes was studied on Ni/Al₂O₃, Co/Al₂O₃, Pd/Al₂O₃, and Pt/Al₂O₃ catalysts and a polymolecular mechanism was proposed. According to this mechanism, a polymolecular intermediate complex is formed from the reactant and catalyst, this complex decomposes in different ways, according to the kinetic conditions, giving the reaction products. The carbon deposition and formation of condensating products during catalysis were also explained according to this mechanism.

In the present work, the heterogeneous catalytic dissociation of methylcyclohexane and cyclohexane over Cu/Al₂O₃ catalyst was studied in flow system under normal pressure. The textural characteristics of the catalyst were also studied.

Experimental

Materials

The copper/alumina catalyst was prepared by impregnation according to the method given by *Kotter and Riekert* [7]. The gel obtained was washed thoroughly, dried at 350 K for 14 h and then crushed, the sieve fraction 0.25—0.50 mm was employed in the surface and catalytic activity measurements.

The methylcyclohexane was provided from laboratory chemicals, and it was found to be chromatographically pure.

The cyclohexane was prepared by keeping the product obtained from the Rectapure Prolabo Laboratory Chemicals over a Linde Va molecular sieve for 72 h and then distilling it at a constant boiling point of 80.3 °C. The distillate was chromatographically pure.

Apparatus and technique

Each catalyst sample was activated *in situ* by calcination at 500 °C for 4 h in a current of dry air free from CO₂ (Cu/AlO) or in a current of pure hydrogen free from H₂O (Cu/AlH). The activated solids were then cooled from the activation temperature to the catalytic reaction temperature. The activation temperature for the catalyst samples was chosen as 500 °C since thermogravimetric analysis indicated that the solid lost its water of crystallization at 450 °C.

The catalytic activity was measured using a flow technique. The reactant was introduced by a microdose pump (Unipan 335 A) and the speed of feeding was varied in the range $(273.0—1092.3) \times 10^{-4} \text{ cm}^3 \text{ min}^{-1}$ and $(276.6—1106.5) \times 10^{-4} \text{ cm}^3 \text{ min}^{-1}$ for methylcyclohexane and cyclohexane, respectively, the reaction temperature being 400—480 °C. The catalyst sample (volume 1 cm³) 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 ± 0.1 °C. The reactor and the furnace were mounted in an inclined position.

The gaseous and liquid products were analyzed in a programmed gas-liquid chromatograph (Pye series 104 programmed chromatograph with a heated dual flame ionization detector) on 2/10 PEGA using pure nitrogen as a carrier gas. Hydrogen was detected by a chromatograph with thermal conductivity detector using nitrogen as a carrier gas.

Measurements and analysis

The adsorption—desorption isotherm of nitrogen at -195 °C was determined using a conventional apparatus [8].

The X-ray diffraction patterns of the catalyst sample and its products after calcination for 4 h at 400, 500, and 750 °C in dry air were obtained using an X-ray diffractometer,

model PW 1050 (Philips) at $\lambda = 1.54 \text{ \AA}$. A $\text{CuK}\alpha$ target with a nickel filter was used. All the diffraction patterns were measured at room temperature; the peak was recorded in a single run.

Results and discussion

Textural characteristics of $\text{Cu}/\text{Al}_2\text{O}_3$ catalyst

The surface area S_{BET} was calculated using the conventional Brunauer—Emmett—Teller (BET) equation [9], and it was found to be $155.5 \text{ m}^2 \text{ g}^{-1}$. This surface area value was compared with the area obtained by the V_t — t method [10, 11].

The adsorption—desorption isotherm of nitrogen at -195°C on the copper/alumina catalyst appears to be type III isotherm of the Brunauer—Deming—Deming—Teller classification [12, 13].

In the X-ray study of the solid sample the d spacing was estimated at each temperature (400, 500, and 750°C) and compared with the values given in the ASTM cards [14]. The results obtained are given in Fig. 1. It follows from Fig. 1 and the ASTM cards that different main peaks appeared at all the calcination temperatures. These peaks indicate the presence of a mixture of copper oxide paratenorite and copper oxide synth cuprite with different formulae $6\text{CuO} \cdot \text{Cu}_2\text{O}$ and $(\text{Cu}_2\text{O})6\text{C}$.

However, the catalyst sample calcined at 750°C contains different peaks which indicate the presence of copper oxide synth tenorite with the formula $(\text{CuO})8\text{N}$.

The crystallite size (t value) was calculated for each sample at 100% intensity by applying the following expression [15] for the breadth in terms of the crystallite size

$$\beta = K\lambda/(t \cos \Theta)$$

where β is the peak width at half-intensity, t is a linear dimension of the crystallite and K is a numerical constant of the order of unity.

It follows that the average crystallite dimension increases with calcination temperature from 0.86 to 1.06 \AA . These findings are in good agreement with those given in Refs. [16, 17].

The heterogeneous kinetic studies

The reaction temperature was monitored at 400°C , and the hydrocarbon vapour was allowed to pass over the catalyst under reaction conditions given

in Experimental. This experiment was repeated at 430, 450, and 480 °C over fresh portions of Cu/Al₂O₃ catalysts pretreated with dry air (Cu/AlO) or with hydrogen (Cu/AlH).

The volume of the gaseous products was determined at various intervals. When this volume was plotted against time a straight line was obtained, the slope of which gave the rate of formation of the gaseous products, which was then corrected to standard temperature and pressure ($Q_V^0/(\text{cm}^3 \text{min}^{-1})$).

The gaseous products were found to be hydrogen and methane in both cases of conversion of cyclohexane and methylcyclohexane. The liquid products of methylcyclohexane conversion were found to be toluene, cyclohexane, cyclohexene, cyclohexadiene, and benzene with unreacted methylcyclohexane (Tables

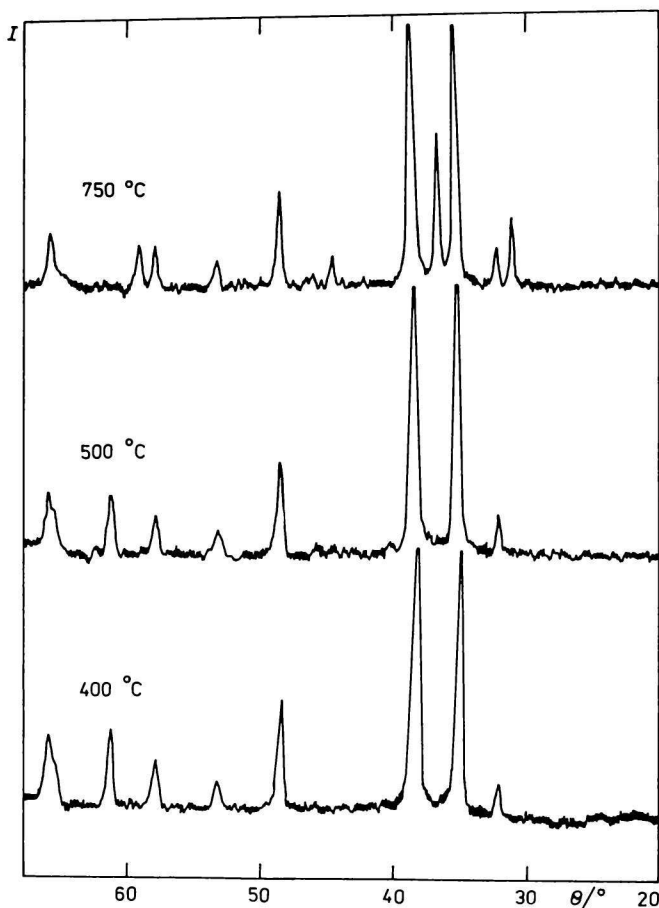








Fig. 1. X-Ray diffraction patterns for Cu/AlO catalyst, thermally treated at 400, 500, and 750 °C.

Table 1







The effect of speed of feeding f on the catalytic conversion of methylcyclohexane on Cu/AlO catalyst in flow system under normal pressure

θ °C	$f \cdot 10^2$ cm ³ min ⁻¹	Q_V^g cm ³ min ⁻¹	α %	ΔE kJ K ⁻¹ mol ⁻¹	$\Delta m(\text{catalyst})$ %	Content of liquid products/%					
											
400	2.73	4.9	3.62	23.5	17.8	0.35	—	2.95	Tr	0.52	96.18
	5.46	4.7	4.48			1.02	—	2.77	Tr	0.69	95.52
	8.19	4.6	3.72			0.93	—	2.57	Tr	0.93	95.57
	10.92	3.5	4.22			0.94	—	2.57	Tr	0.94	95.78
430	2.73	7.6	10.20	23.5	14.1	1.33	4.88	3.10	Tr	0.89	89.80
	5.46	7.6	10.22			0.88	5.44	3.81	Tr	0.09	89.78
	8.19	7.3	8.68			1.20	3.52	2.64	Tr	1.32	91.32
	10.92	7.2	8.27			1.32	3.86	2.21	Tr	0.88	91.73
450	2.73	8.3	14.90	23.5	13.2	2.31	5.13	5.63	Tr	1.83	85.10
	5.46	8.0	12.83			2.18	5.26	4.51	Tr	0.88	87.17
	8.19	8.0	9.45			2.11	3.54	2.92	Tr	0.88	90.55
	10.92	7.3	9.33			0.80	3.54	2.33	Tr	1.77	90.67
480	2.73	9.1	15.86	23.5	12.6	2.63	7.35	5.25	Tr	0.63	84.14
	5.46	9.1	14.16			2.62	6.37	4.62	Tr	0.55	85.84
	8.19	8.9	11.87			1.66	4.55	4.55	Tr	1.11	88.13
	10.92	8.9	14.39			0.85	7.40	5.29	Tr	0.85	85.61

Tr — traces. Q_V^g — flow rate of gaseous products.

Table 2

The effect of speed of feeding f on the catalytic conversion of methylcyclohexane on Cu/AlH catalyst in flow system under normal pressure

θ °C	$f \cdot 10^2$ cm ³ min ⁻¹	Q_V^0 cm ³ min ⁻¹	α %	ΔE kJ K ⁻¹ mol ⁻¹	$\Delta m(\text{catalyst})$ %	Content of liquid products/%					
											
400	2.73	5.9	7.19	26.81	12.6	Tr	3.00	2.51	0.42	1.26	92.81
	5.46	5.9	6.39			Tr	2.50	2.26	0.49	1.14	93.61
	8.19	5.4	7.65			Tr	2.70	3.30	0.33	1.32	91.35
	10.92	5.8	5.06			Tr	1.00	2.80	0.63	0.63	94.94
430	2.73	6.3	11.83	26.81	10.7	Tr	3.50	4.26	0.81	3.26	88.17
	5.46	6.2	8.73			Tr	2.90	3.77	0.96	1.10	91.27
	8.19	5.6	7.22			Tr	3.20	2.30	0.72	2.00	92.78
	10.92	5.8	8.82			Tr	3.70	2.89	0.51	1.72	91.18
450	2.73	7.7	12.66	26.81	13.6	Tr	4.60	4.10	0.85	3.11	87.34
	5.46	7.9	9.82			Tr	2.63	4.89	0.83	1.47	90.18
	8.19	7.4	7.09			Tr	2.20	2.62	0.62	1.65	92.91
	10.92	7.0	10.51			Tr	3.90	4.60	0.98	1.03	89.49
480	2.73	11.8	12.88	26.81	12.8	Tr	4.50	4.49	1.07	2.83	87.12
	5.46	10.8	10.55			Tr	2.90	4.53	1.20	1.92	89.45
	8.19	11.5	8.17			Tr	3.40	2.48	0.52	1.77	92.83
	10.92	11.8	11.70			Tr	3.90	4.25	0.81	2.74	88.31

1 and 2). The liquid products of cyclohexane conversion were found to be benzene and cyclohexene with unreacted cyclohexane.

In all cases of the decomposition of methylcyclohexane and cyclohexane the rate of formation of gaseous products and the conversion ($\alpha/\%$) of the hydrocarbons were independent of their rates of flow (Figs. 2 and 3), *i.e.* the rate of reaction was independent of the speed of feeding or the contact time. This indicates that the reaction of methylcyclohexane and cyclohexane on copper/alumina catalyst, pretreated with air or hydrogen at 500 °C, is taking place on a surface completely covered with adsorbed molecules of hydrocarbon. This situation is quite different from Henry's region characterized by incomplete surface coverage. Consequently, the reaction of decomposition of hydrocarbons, under the present experimental conditions, is of the zero order.

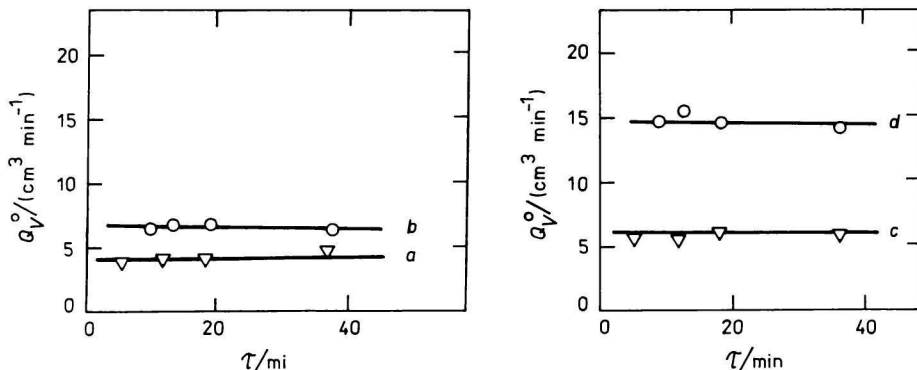


Fig. 2. Effect of variation of time of contact τ on the conversion of methylcyclohexane (a) and cyclohexane (b) on Cu/AlO catalyst at 400 °C and methylcyclohexane (c) and cyclohexane (d) on Cu/AlH catalyst at 450 °C.

It is known [18] that heterogeneous reactions proceed in more than one step. The main steps in a heterogeneous catalytic process are: diffusion from the gaseous phase to the catalyst surface, adsorption on the catalyst surface, surface reaction, desorption, diffusion of the desorbed species from the catalyst surface to the gaseous phase.

Preliminary experiments using different particle sizes of the copper/alumina catalyst (from 0.25 to 1 mm in diameter) showed that the reaction rates of decomposition of methylcyclohexane and cyclohexane were independent of the particle size of the catalyst, therefore, the rate-determining step is neither the rate of diffusion of the reactant molecules to the catalyst surface, nor the rate of diffusion of the desorbed species from the catalyst surface to the gaseous

phase. Also, on the basis of molecular calculations, the equilibrium is attained very fast between the adsorption and desorption species, this indicates that neither the rate of adsorption, nor the rate of desorption is the rate-determining step. Consequently, the rate-determining step is the rate of one of the surface reactions.

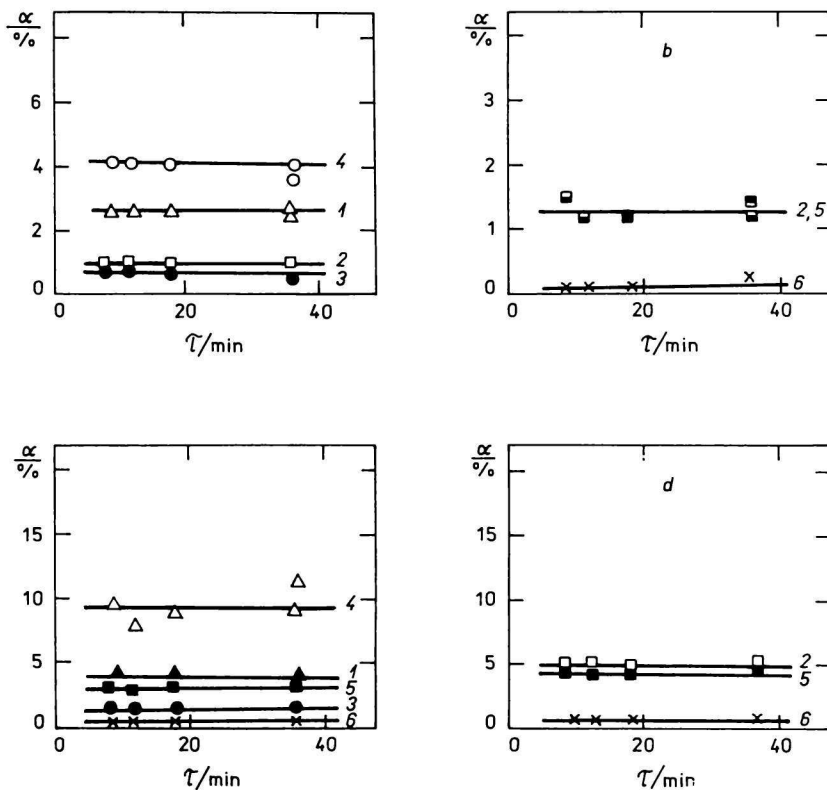


Fig. 3. Effect of variation of time of contact on the formation of the products of conversion of methylcyclohexane (a) and cyclohexane (b) on Cu/AlO catalyst at 400 °C and methylcyclohexane (c) and cyclohexane (d) on Cu/AlH catalyst at 450 °C.

1. Cyclohexadiene; 2. cyclohexane; 3. toluene; 4. methylcyclohexane; 5. cyclohexene; 6. benzene.

It should be noticed that the mass of the catalyst was found to increase after using it in the hydrocarbons conversion. The apparent gain in mass of the catalyst, after the course of rate determination (2 h), is given in Tables 1—4. For methylcyclohexane conversion over Cu/AlO catalyst the apparent gain in mass was found to decrease, but it was almost constant in its conversion over Cu/AlH catalyst, with respect to temperature. For cyclohexane conversion the apparent

Table 3

The effect of speed of feeding f on the catalytic conversion of cyclohexane on Cu/AIO catalyst in flow system under normal pressure







θ °C	$f \cdot 10^2$ cm ³ min ⁻¹	Q_V^0 cm ³ min ⁻¹	α %	ΔE kJ K ⁻¹ mol ⁻¹	$\Delta m(\text{catalyst})$ %	Content of liquid products/%		
								
400	2.76	6.1	1.54	35.3	6.8	1.15	0.39	98.46
	5.53	6.5	1.11			1.11	Tr	98.89
	8.29	6.4	1.09			1.09	Tr	98.91
	11.06	5.9	1.61			1.61	Tr	98.39
430	2.76	9.1	3.44	35.3	11.4	2.67	0.77	96.56
	5.53	8.8	2.62			1.83	0.79	97.38
	8.29	8.4	2.11			1.41	0.70	97.89
	11.06	8.6	2.78			2.49	0.29	97.22
450	2.76	11.7	3.80	35.3	18.9	2.85	0.95	96.20
	5.53	12.9	3.21			2.61	0.60	96.79
	8.29	12.3	2.99			2.24	0.75	97.01
	11.06	12.9	3.29			2.54	0.75	96.71
480	2.76	13.1	11.14	35.3	15.4	7.99	3.15	88.86
	5.53	13.1	10.25			7.96	2.56	89.75
	8.29	14.8	8.40			6.22	2.18	91.60
	11.06	13.5	7.90			6.25	1.64	92.10

Table 4

The effect of speed of feeding f on the catalytic conversion of cyclohexane on Cu/AlH catalyst in flow system under normal pressure

θ °C	$f \cdot 10^2$ cm ³ min ⁻¹	Q_V^0 cm ³ min ⁻¹	α %	ΔE kJ K ⁻¹ mol ⁻¹	$\Delta m(\text{catalyst})$ %	Content of liquid products/%		
								
400	2.76	6.5	2.20	35.3	5.2	2.20	Tr	97.80
	5.53	6.7	2.00			2.00	Tr	98.00
	8.29	6.3	1.97			1.97	Tr	98.03
	11.06	6.1	1.80			1.80	Tr	98.20
430	2.76	7.9	2.60	35.3	12.3	2.60	Tr	97.40
	5.53	7.8	3.70			3.70	Tr	96.30
	8.29	9.1	3.00			3.00	Tr	97.00
	11.06	8.2	2.40			2.40	Tr	97.60
450	2.76	14.2	4.53	35.3	10.3	4.30	0.23	95.47
	5.53	14.7	4.27			4.04	0.23	95.73
	8.29	15.2	4.80			4.29	0.51	95.20
	11.06	14.8	4.20			3.98	0.22	95.80
480	2.76	17.8	5.02	35.3	10.3	4.65	0.37	94.98
	5.53	20.8	4.85			4.50	0.35	95.15
	8.29	20.1	4.93			4.63	0.30	95.07
	11.06	20.9	4.70			4.40	0.30	95.30

gain in mass of the catalyst was found to increase after the course of rate determination with respect to temperature in both cases of Cu/AlO and Cu/AlH catalysts.

The effect of reaction temperature was investigated in connection with the determination of the apparent activation energy. A plot of $\log(\alpha/\%)$ (at the different flow rates, at various temperatures between 400 and 480 °C) vs. $1/T$ (T is the absolute working temperature), allowed us to calculate the apparent activation energy of conversion of methylcyclohexane and cyclohexane (Figs. 4 and 5). Tables 1—4 include the calculated activation energies ΔE for the conversion of methylcyclohexane and cyclohexane over Cu/AlO and Cu/AlH catalysts at each speed of feeding.

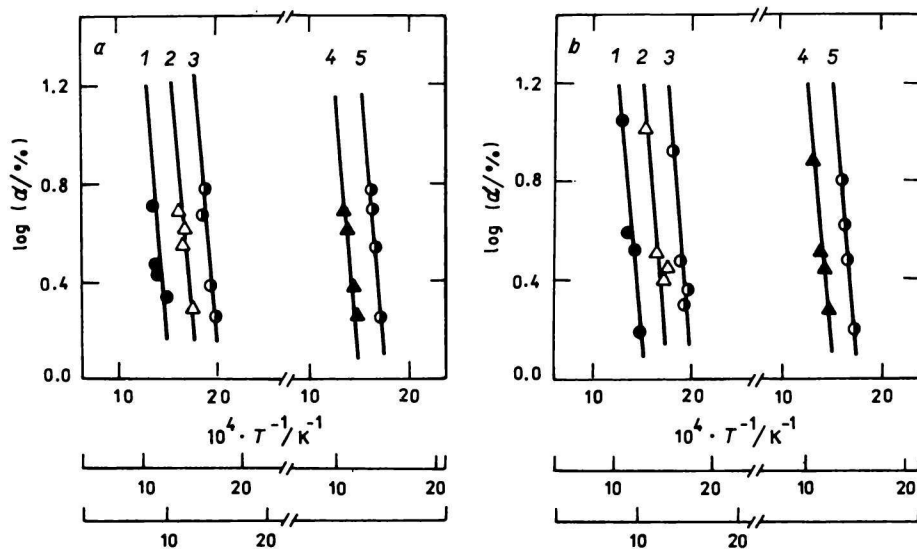
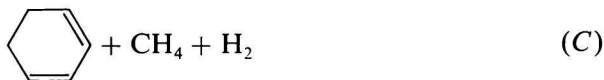
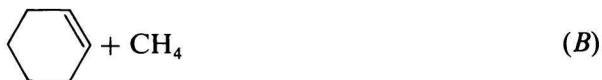


Fig. 4. Effect of temperature on the catalytic conversion of cyclohexane on a) Cu/AlO catalyst and b) Cu/AlH catalyst at $f = 10^4 / (\text{cm}^3 \text{min}^{-1})$: 1. 276.6, 2. 553.2, 3. 829.8, 4. 1106.5, 5. 276.6.

It is evident from the values of the apparent activation energy ΔE that it is almost independent of the contact time, the working time of the catalyst, and the pretreatment gas.

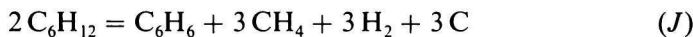
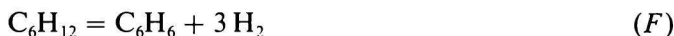
It can be concluded then that the heterogeneous catalytic dehydrogenation of the hydrocarbons on copper/alumina catalyst is not a simple catalytic process under the present experimental conditions.

The possibilities for the conversion of methylcyclohexane to different products are as follows



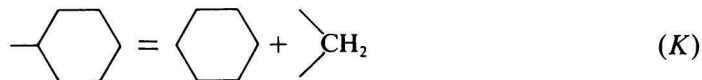
These possible products are actually known for the heterogeneous catalytic conversion of methylcyclohexane over different catalysts [18].

Also, the following possibilities are known for the conversion of cyclohexane



These products are actually formed in the conversion of cyclohexane over different catalysts [19—21] (nickel/alumina, platinum/alumina, and palladium/alumina).

Process (A) may also be represented as



which suggests the formation of methylene radical [22]. However, this formation needs vigorous conditions (high temperature and pressure), which is not satisfied in our experiment. Moreover, the amount of cyclohexane formed is not sufficient, in all cases, to indicate the formation of methylene radicals. Also, if methylene radicals are formed different alkyl products of benzene would be observed, which is not the case under our experimental conditions.

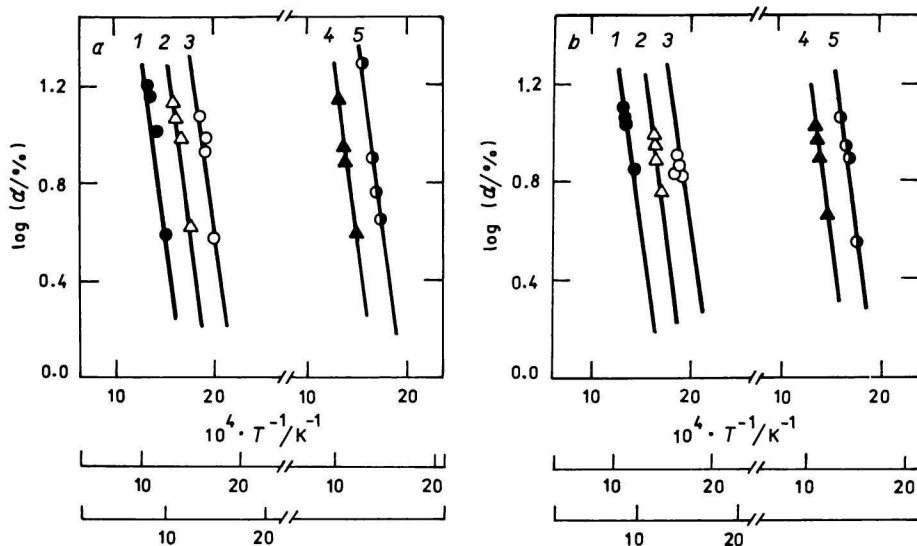


Fig. 5. Effect of temperature on the catalytic conversion of methylcyclohexane on a) Cu/AlO catalyst and b) Cu/AlH catalyst at $f \cdot 10^4 / (\text{cm}^3 \text{min}^{-1})$: 1. 273.0, 2. 546.1, 3. 819.2, 4. 1092.3, 5. 273.0.

The results of the present investigation were plotted on coordinates of Balandin's equation (Fig. 6)

$$2.303f \log(1 - Y)^{-1} = \alpha + \beta f Y$$

which was derived for monomolecular catalytic processes proceeding over a catalyst surface completely covered by adsorbed molecules, through the formation of an intermediate monomolecular catalytic complex, which immediately decomposes to give the reaction products. In this equation f is the speed of feeding of reactant substance, Y is the conversion ratio, α and β are constants independent of f . It follows from Fig. 6 that the obtained results correspond to the Balandin's equation [23] and linear straight lines were obtained.

However, on calculating the relative adsorption coefficients under the conditions of investigation, they had no physical meaning. It seems therefore that the processes of conversion of methylcyclohexane and cyclohexane over copper/alumina catalyst under the conditions of investigation may not be due to the formation of monomolecular catalytic complex, but to the formation of an intermediate, a catalytic complex, having different character.

Accordingly, the polymolecular mechanism is suggested for the conversion of methylcyclohexane and cyclohexane on copper/alumina catalyst, through the formation of a polymolecular catalytic complex as an intermediate, formed from the condensation of hydrocarbon molecules on the catalyst surface, which

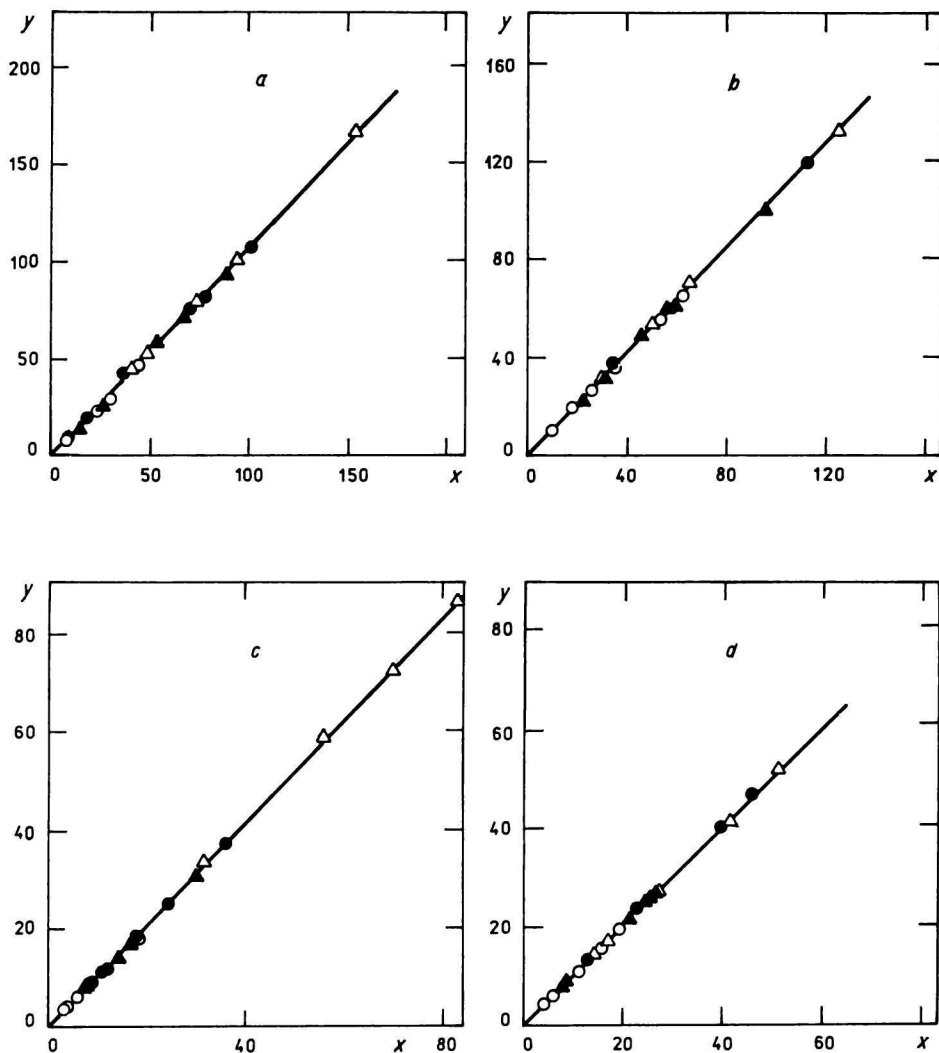


Fig. 6. Balandin kinetic equation for the conversion of methylcyclohexane on Cu/AlO catalyst (a) and Cu/AlH catalyst (b) and of cyclohexane on Cu/AlO catalyst (c) and Cu/AlH catalyst (d).

● 400 °C; △ 430 °C; ○ 450 °C; ▲ 480 °C.

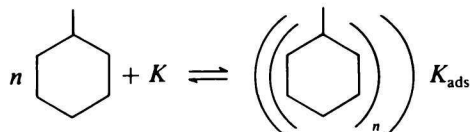
Axis $x = fY \cdot 10^{-4}$, $y = 2.303f \log(1 - Y)^{-1} \cdot 10^{-4}$

immediately decomposes in different ways depending on the kinetic conditions and on the nature of the catalyst used.

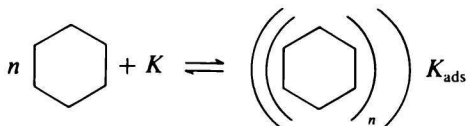
The polymolecular mechanism of conversion of alcohols on alumina was discussed previously [24, 25].

According to [26—28], the polymolecular mechanism is more probable in organic heterogeneous catalytic reactions when the reaction is accompanied by the formation of polymerization and polycondensation products.

The formation of the polymolecular intermediate may be represented as



for methylcyclohexane conversion, and

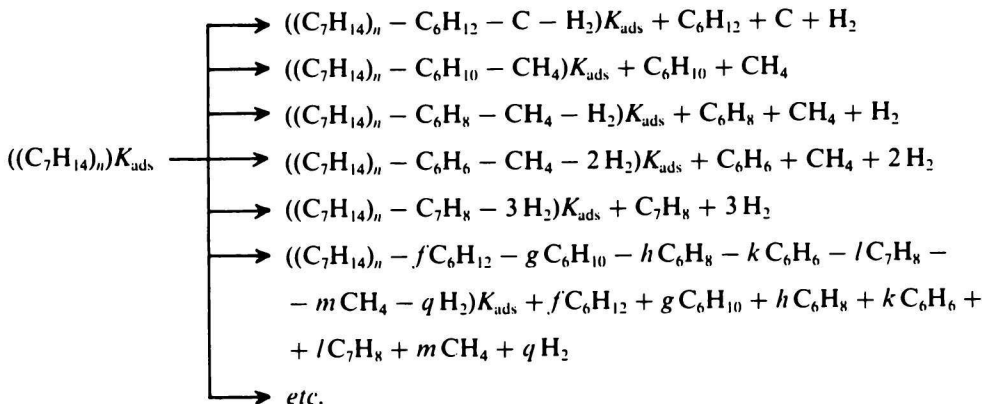


for cyclohexane conversion, where *K* indicates the catalyst surface. This intermediate decomposes immediately in several ways giving the different products.

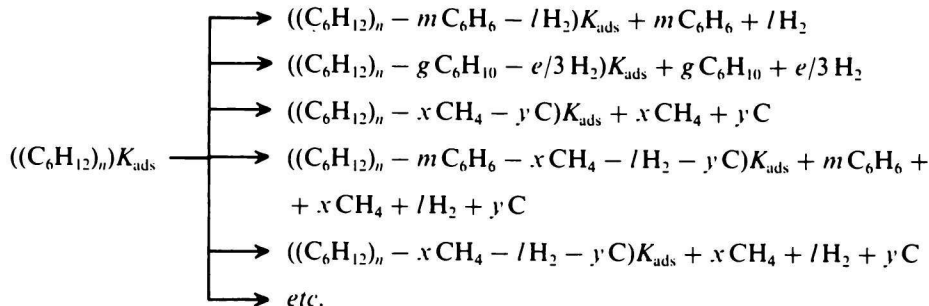
Scheme 1 shows the formation of the different products of conversion of methylcyclohexane by the decomposition of the intermediate, a polymolecular catalytic complex.

For cyclohexane conversion, the decomposition of the complex to products is represented by Scheme 2.

Schemes 1 and 2 account for the presence of the different products, and for the increase in the mass of the catalyst, since it is known [26] that benzene can form condensation products which may cover the catalyst surface, or at least the active part of it, giving rise to an increase in the catalyst mass.



Scheme 1



Scheme 2

References

1. Anderson, J. R. and Baudert, M., *Catalysis. Science and Technology*. Vol. I. Academic Press, London, 1981.
2. Shuykin, N. I., Minachev, K. H. M., Feofanova, L. M., Treshchova, E. G., Yudkina, T. P., and Agronov, A. E., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1955, 11; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 9, 441 (1955).
3. Ezzo, E. M., Youssef, N. A., and Ali, S. A., *J. Surf. Tech.* 14, 177 (1981).
4. Ezzo, E. M., Youssef, N. A., and El-Aiashy, M. K., *J. Surf. Tech.* 20, 111 (1983).
5. Ezzo, E. M. and Rudenko, A. P., *J. Surf. Tech.* 9, 43 (1979).
6. Ezzo, E. M., Youssef, N. A., and El-Kherbawi, M. A., *Arab Gulf J. Sci. Res.* 2 (1), 45 (1984).
7. Kotter, M. and Riekert, I., private communication.
8. Joyner, L. G., *Scientific and Industrial Glass Blowing*. (Barr, W. E. and Anhorn, J. V., Editors.) P. 275. Instrument Publishing Co., Pittsburry, 1949.
9. Brunauer, S., Emmett, P. H., and Teller, E., *J. Am. Chem. Soc.* 60, 369 (1938).
10. Lippens, B. C., Linsen, B. G., and de Boer, J. H., *J. Catal.* 4, 38 (1965).
11. Lippens, B. C. and de Boer, J. H., *J. Catal.* 4, 319 (1965).
12. Dubinin, M. M., Zavrina, E. D., and Radushkevich, L. V., *Zh. Fiz. Khim.* 21, 1351 (1947).
13. Gregg, S. J. and Sing, K. S. W., *Adsorption, Surface Area and Porosity*, p. 3. Academic Press, New York, 1982.
14. Powder Diffraction File, Alphabetical Index, *Inorganic Compounds*. International Centre for Diffraction Data, Swarthmore, PA, 1978.
15. Fitton, B. and Griffith, C. H., *J. Appl. Phys.* 39, 3663 (1968).
16. Basolo, F. and Burwell, R. L., Jr., *Catalytic Progress in Research, Proc. NATO Science Committee Conf. on Catalysis*. Santa Margherita di Pula, December, 1972. Department of Chemistry, Northwestern University, Evanston IL, 1972.
17. Draughlis, E. and Jaffe, R. I., *The Physical Basis for Heterogeneous Catalysis*. Plenum Press, New York, 1975.
18. Kiperman, S. L., *Introduction in Kinetics of Heterogeneous Catalytic Reactions*, p. 125. Izd. Nauk, Moscow, 1964.
19. Balandin, A. A., *Zh. Russ. Fiz. Khim., Chast' Khim.* 61, 909 (1929).
20. Braude, E. A., Linstead, R. P., and Mitchell, P. W., *J. Chem. Soc.* 1954, 3578.
21. Shopov, D. and Andreev, A. A., *Izd. Otd. Khim. Nauki, Bulg. Akad. Nauk* 2 (3), 583 (1970).
22. Zelinskii, N. D. and Shuykin, N. I., *Dokl. Akad. Nauk SSSR* 3, 255 (1934).

23. Balandin, A. A., *Adv. Catal. Relat. Subj.* 10, 102 (1958).
24. Ezzo, E. M., Balandin, A. A., and Rudenko, A. P., *Kinet. Katal.* 9, 1101 (1968).
25. Rudenko, A. P. and Ezzo, E. M., *Kinet. Katal.* 11, 1064 (1970).
26. Rudenko, A. P., *DrSc. Thesis*, Moscow University, 1971.
27. Balandin, A. A., *Zh. Fiz. Khim.* 31, 645 (1957).
28. Rudenko, A. P., in *Sovremennye problemy fizicheskoi khimii*. (Up to Date Problems of Physical Chemistry.) Vol. 3, p. 263. Izd. Moskovskogo universiteta, Moscow, 1968.