

**Investigation of the Heterogeneous Catalytic
Conversion of Cycloalkanes on Ni-Al₂O₃/α-Al₂O₃ Catalyst
Part II. The Disproportionation of Cyclohexene**

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ABSTRACT. In a previous study (Ali and Mazhar 1991) the kinetics of the heterogeneous catalytic conversion of cyclohexane was studied on Ni-Al₂O₃/α-Al₂O₃ catalyst in flow system under normal pressure. Owing to the different products obtained and to the increase in the mass of the catalyst the polymolecular mechanism was suggested, and the catalytic activity was found to improve on supporting the impregnated nickel alumina on α-alumina. Among the obtained products was cyclohexene, it seemed of interest to study the kinetics of the heterogeneous conversion of cyclohexene on the same catalyst, under the same experimental conditions.

The study revealed that the conversion of cyclohexene is a zero-order reaction and that the apparent activation energy for the reaction has a value of 18.4 kcal mol⁻¹. The effects of pretreatment conditions and of the nature of the catalyst on the conversion were studied.

The polymolecular mechanism was suggested for the conversion of cyclohexene over Ni-A/A catalyst under our experimental conditions.

The disproportionation process as a direct intermolecular hydrogen transfer between three adsorbed molecules, simultaneously was explained by Balandin (Balandin 1969).

The mechanism of direct intermolecular hydrogen transfer was supported by different investigations on various catalysts (Greaznov 1963).

The effect of the support on the surface properties of the catalyst was studied in many investigations. The surface chemical properties of precipitated nickel oxide/aluminium oxide-silicon dioxide catalysts with different compositions and the corresponding aluminium-silicon dioxide carriers were studied (Wendt *et al.* 1985).

The influence of thorium on the state and dispersion of nickel oxide supported on silicon dioxide and on γ -alumina was investigated (Ledford *et al.* 1984). And the effects of metal loading and support materials on the surface properties of supported cobalt catalysts were studied for different support materials (Choi *et al.* 1983.)

The influence of the Ni content and the calcination temperature on the interaction between nickel oxide and aluminium oxide was examined, and a very effective interaction was present between the support and the active phase (De Korte *et al.* 1985).

Also the activity and selectivity of nickel / γ -alumina catalyst denatured with antimony was studied in the dehydrogenation of cyclohexane (Nguyen *et al.* 1984).

These several investigations indicate how interesting and important is studying the influence of the support on the behaviour of the catalyst.

In our investigation the heterogeneous kinetics of the catalytic conversion of cyclohexene was studied over nickel-alumina supported on α -alumina at a temperature range 400-480°C using a flow technique under normal pressure.

1. Experimental Details

1.1 Materials

The nickel-alumina supported on alumina (31.1% Ni by wt) solid catalyst (Ni-A/A) was prepared following the method given in ref. (Ali and Mazhar 1991).

The cyclohexene (b.p. 80°C) was obtained as in ref. (Ezzo *et al.* 1981) and was chromatographically pure.

1.1i. Apparatus

The adsorption-desorption isotherm of nitrogen at -195°C was determined using a conventional apparatus (Joyner 1949).

The X-ray diffraction analysis was carried out using a philips model PW 1050 X-ray diffractometer at $\lambda = 1.54 \text{ \AA}$. Using a Cu K_{α} target with a nickel filter.

The catalytic activity was measured using a flow technique consisting of a micro dose pump (Unipan 335 A), and a silica tube reactor with an internal diameter of 12 mm introduced into a tube which is inserted in a tubular furnace (Rock A) mounted in an inclined position, the temperature of which is controlled to $\pm 0.1^{\circ}\text{C}$.

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

Hydrogen was detected by a chromatograph with thermal conductivity detector using nitrogen as a carrier gas.

1.1.ii. Techniques

The specific surface area of the catalyst was determined by means of nitrogen sorption technique at -195°C . The sample was outgassed at 300°C for 3hr under a reduced pressure of 10^{-5} Torr before any adsorption measurement was made.

The X-ray diffraction patterns of the solid sample and its products after calcination at 400, 500 and 750°C in dry air were measured at room temperature, the peak was recorded in a single run.

In the kinetic study, series of experiments were carried out, in which the temperature was kept constant at 400°C and the space velocity was adjusted at 9.4×10^{-2} , 12.7×10^{-2} , 15.4×10^{-2} and 17.8×10^{-2} respectively, to study the effect of space velocity (f) and time of contact (t) on the conversion process. The same procedure was repeated at 430, 460 and 480°C , to study the effect of temperature.

The solid sample (volume 1 ml) was introduced into the silica reactor and was activated in situ by calcination at 500°C for 4hr in a current of dry air free from CO_2 (Ni-A/AO), or in a current of dry hydrogen free from H_2O (Ni-A/AH). The activated catalyst was then cooled from the activation temperature to the catalytic reaction temperature. The activation temperature was chosen to be 500°C since thermogravimetric analysis showed that the catalyst Ni-A/A lost its water of crystallization and water of hydroxylation at 452°C . The cyclohexene was allowed to flow at the previous flow rates over the catalyst, and the volume of the gaseous products was determined at various time intervals, this volume when plotted against time gave a straight line whose slope gave the rate of formation of the gaseous products (V , ml/min), which was then calculated at STP (V° , ml/min).

2. Results and Discussion

2.1 Textural characteristics of Ni-A/A catalysts

The surface area S_{BET} was calculated using the conventional Brunauer-Emmett-Teller (BET) equation (Brunauer *et al.* 1938), as in ref. (Ali and Mazhar 1991) and was found to be $152 \text{ m}^2\text{g}^{-1}$.

2.2. X-ray study of the solid samples

The d spacing was estimated at each temperature (400° , 500° and 750°C) and compared with the values given in the ASTM cards (Powder Diffraction File 1978), and was given in (Ali and Mazhar 1991).

2.3. Effect of space velocity (*f*)

The analyses indicated the presence of hydrogen and methane as gaseous products, cyclohexane and benzene as liquid products together with unreacted cyclohexene.

Fig. (1) shows the effect of variation in time of contact (1/space velocity) on the rate of conversion of cyclohexene at 480°C, and on the rate of formation of gaseous products V° at 400, 430, 460 and 480°C [(a) over Ni-A/AO and (b) over Ni-A/AH catalysts].

It follows from this figure that the rate of formation of gaseous products and the percentage conversion of cyclohexene are independent of its rate of flow, *i.e.* the conversion of cyclohexene is a zero-order reaction; which means that the catalyst surface, or at least the active part of it is saturated with chemisorbed molecules.

It is clear from the analysis of the gaseous and liquid products that beside the disproportionation of cyclohexene to cyclohexane and benzene,



there are other processes that take place in the heterogeneous catalytic conversion of cyclohexene under the experimental conditions.

It is evident from Fig (2) that the rates of formation of benzene and cyclohexane are independent of the rate of flow of cyclohexene, *i.e.* zero order reactions.

2.4. Effect of the reaction temperature (determination of the apparent activation energy)

From the data of $\log V^\circ$ at the various temperatures and space velocities it was possible to calculate the apparent activation energy ΔE of conversion of cyclohexene over Ni-A/A catalyst (Fig. 3 and Tables 1 & 2), and it was found to have an average value of 18.4 kcal mol⁻¹. The apparent activation energy was found to be independent of the contact time, the working time of the catalyst and the pretreatment gas.

For studying the effect of the pretreatment conditions on the catalytic behaviour of the catalyst, the activity and selectivity of Ni-A/AO and Ni-A/AH catalysts (pretreated with dry air and hydrogen respectively) were compared at the maximum and the minimum of the range of temperature under investigation, (*i.e.* at 400 and 480°C). At 400°C, Ni-A/AO catalyst showed less activity towards formation of gaseous products and hydrogenation to cyclohexane and more activity towards dehydrogenation to benzene than Ni-A/AH catalyst. At 480°C, Ni-A/AO showed less activity towards the formation of cyclohexane and benzene and less activity towards the formation of gaseous products than Ni-A/AH catalyst, Table 3.

Table 1. The effect of space velocity f on the catalytic conversion of cyclohexene on Ni-A/AO catalyst in flow system under normal pressure

Temp °C	$f \cdot 10^2$ min ⁻¹	V^o ml min ⁻¹	Conv %	ΔE kJ k ⁻¹ mol ⁻¹	%Gain in wt. (in 2hr)	Analysis of liquid products		
						%		
								
400	9.4	3.35	1.75	18.4	16.92	1.11	0.59	96.85
	12.7	2.89	1.62			1.00	0.57	97.13
	15.4	3.07	1.43			1.03	0.36	97.38
	17.8	2.79	0.46			0.14	0.31	98.54
430	9.4	6.01	1.18	18.4	12.51	0.29	0.86	97.17
	12.7	5.74	0.75			0.11	0.62	97.75
	15.4	5.55	1.08			0.21	0.84	97.37
	17.8	5.74	0.92			0.18	0.72	97.73
460	9.4	11.25	3.76	18.4	21.53	0.88	2.70	96.42
	12.7	11.44	3.56			0.89	2.55	96.56
	15.4	11.62	3.70			0.79	2.78	96.42
	17.8	11.25	2.92			0.49	2.35	97.16
480	9.4	19.58	5.70	18.4	54.61	3.60	1.80	94.60
	12.7	19.20	5.72			3.64	1.77	94.59
	15.4	18.83	4.79			3.33	1.24	95.43
	17.8	18.45	4.74			3.38	1.15	95.47

Table 2. The effect of space velocity f on the catalytic conversion of cyclohexene on Ni-A/AH catalyst in flow system under normal pressure.

Temp °C	$f \cdot 10^2$ min ⁻¹	V^o ml min ⁻¹	Conv %	ΔE kJ k ⁻¹ mol ⁻¹	%Gain in wt. (in 2hr)	Analysis of liquid products		
						%		
								
400	9.4	5.29	3.70	18.4	9.26	3.3	0.25	96.43
	12.7	5.27	3.27			2.9	0.25	96.86
	15.4	5.26	2.09			2.1	Tr	96.95
	17.8	5.25	3.70			2.2	Tr	97.85
430	9.4	11.28	15.15	18.4	67.57	7.5	5.7	86.84
	12.7	10.19	6.83			4.7	1.7	95.26
	15.4	10.01	4.13			1.3	2.6	96.89
	17.8	7.83	1.47			0.8	0.6	96.20
460	9.4	14.60	13.96	18.4	74.77	11.4	0.82	87.76
	12.7	15.06	4.97			4.3	0.49	95.26
	15.4	15.16	3.21		69.8	2.8	0.34	96.89
	17.8	14.33	1.83			3.8	Tr	96.20
480	9.4	26.91	19.62	18.4	69.8	10.99	5.4	83.60
	12.7	27.00	16.00			11.14	2.7	86.21
	15.4	27.20	15.99			11.14	2.7	86.21
	17.8	26.80	15.58			10.81	2.7	86.51

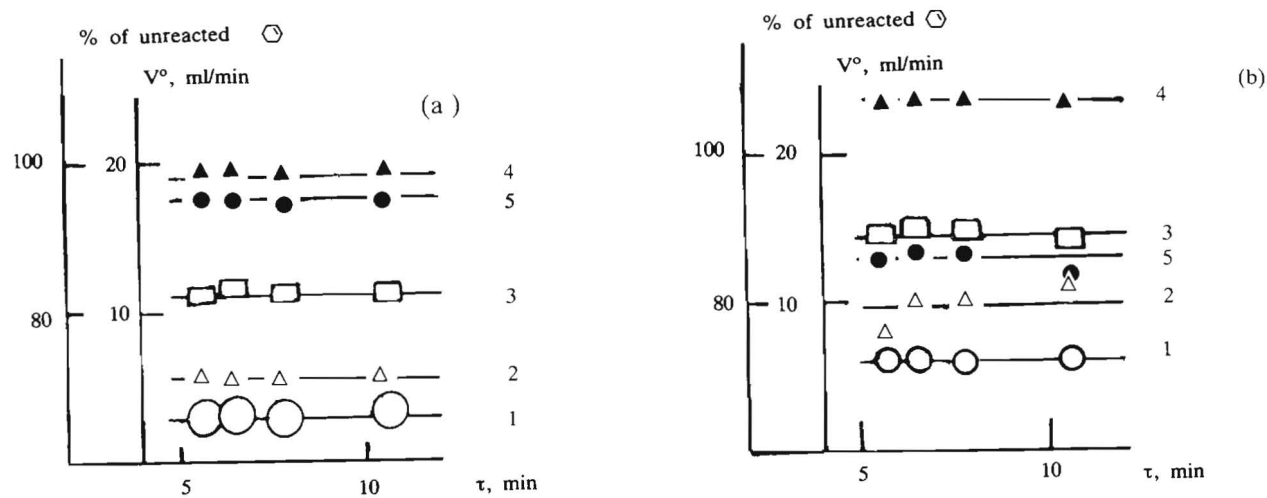


Fig. 1. The effect of variation in time of contact on the rate of conversion of cyclohexene at 480°C (●), and on the rate of formation of gaseous products V° at: 400°C (○), 430°C (△), 460°C (□) and 480°C (▲) over
a) Ni-A/AO b) Ni-A/AH catalyst.

For studying the effect of the nature of the catalyst, a comparison was done between the specific activity of a previously prepared nickel-alumina catalyst (Ezzo *et al.* 1981) (Ni-A catalyst prepared by coprecipitation) and the specific activity of the nickel-alumina/ α -alumina catalyst under investigation. The activities of the two solids (pretreated by hydrogen at 500°C) were calculated, as the amount of each product per gram per surface area, at 400°C. Table (4) includes the calculated values for each catalyst. It is evident that the specific activity of the previously prepared nickel-alumina is higher, this may be due to the large amount of condensating products formed on the surface of the nickel-alumina/ α -alumina (resulting in the increase of the weight of the catalyst after the experiment) giving rise to the shielding of active surface and decreasing the activity. Also due to the higher activation energy of the conversion over nickel-alumina/ α -alumina than over nickel-alumina (18.4 and 16.4 kcal mol⁻¹ respectively).

These comparisons show the dependence of the conversion process on the pretreatment conditions and on the nature of the catalyst, and show the disorder of its stoichiometry.

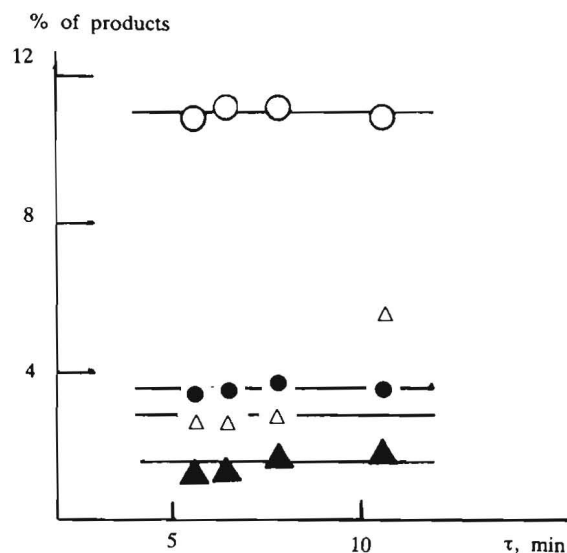


Fig. 2. The effect of variation in time of contact on the rate of formation of the products of the conversion of cyclohexene over Ni-A/A catalyst, at 480°C.

(●) % of cyclohexane and (▲) % of benzene formed in the conversion over Ni-A/AO catalyst, (○) % of cyclohexane and (△) % of benzene formed in the conversion over Ni-A/AH catalyst.

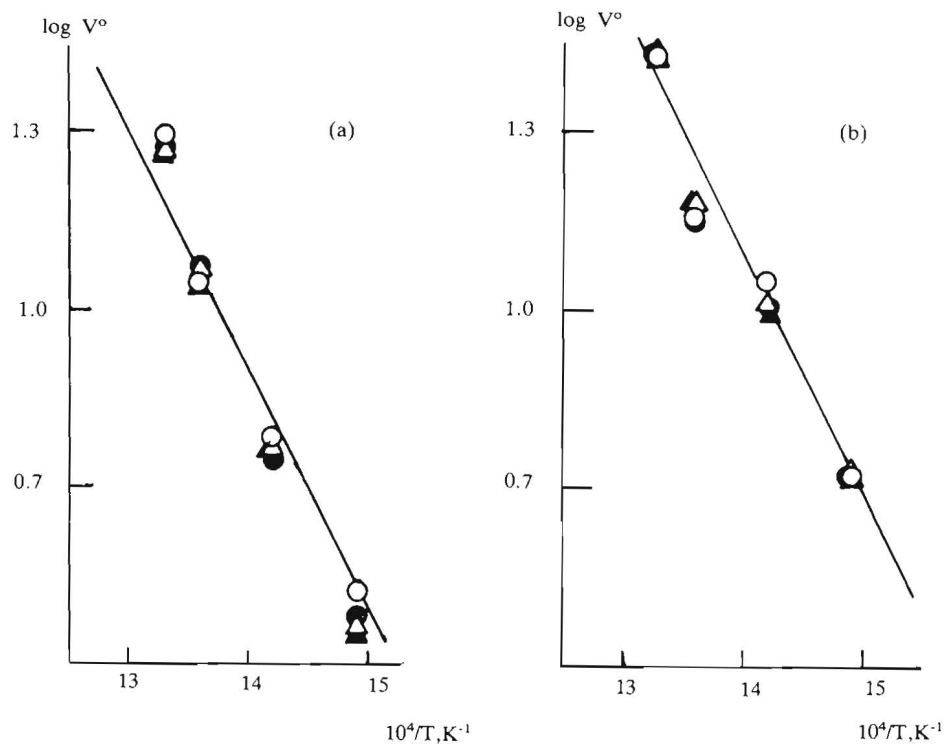


Fig. 3. The effect of temperature on the catalytic conversion of cyclohexene over:

a) Ni-A/AO catalyst

b) Ni-A/AH catalyst

at $f \times 10^{-2}$ ($\circ$) 9.4 min^{-1}

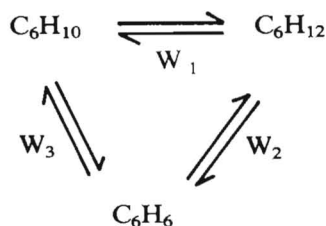
($\triangle$) 12.7 min^{-1}

($\blacktriangle$) 17.8 min^{-1}

($\bullet$) 15.4 min^{-1}

Experiments on particles of the catalyst with different sizes showed no effect on the rate of the conversion, this indicates that the rate determining step is not the rate of diffusion of reactants to the catalyst surface nor the rate of diffusion of products from the catalyst surface.

It is known that benzene is formed directly from cyclohexene and/or indirectly from cyclohexane :



where w_1 , w_2 and w_3 are the rates of reactions.

In previous studies (Ezzo *et al.* 1981, 1984) the effect of the presence of cyclohexane and benzene on the catalytic conversion of cyclohexene over nickel-alumina catalyst was investigated using artificial mixtures of cyclohexene-benzene and cyclohexene-cyclohexane prepared with different mole fractions. The results obtained gave an information about the influence of the reaction products on the catalytic conversion of cyclohexene. It was found that the presence of benzene increases the rate of dehydrogenation of cyclohexene whereas it decreases the rate of hydrogenation, on the other hand the presence of cyclohexane increases the rate of dehydrogenation of cyclohexene.

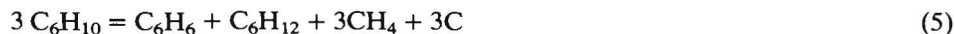
Table 3. The activity and selectivity of the nickel-alumina supported on α -alumina catalyst in heterogeneous catalysis of cyclohexene

Temp	V%/g		 %/g		 %/g	
°C	O	H	O	H	O	H
400	2.54	4.88	0.69	2.42	0.38	0.12
430	12.8	7.86	0.43	2.87	1.68	2.13
460	9.57	12.02	0.64	4.52	2.18	0.33
480	14.63	21.41	2.68	8.75	1.15	2.66

Table 4. The activities of Ni-AH and Ni-A/AH catalysts in the heterogeneous catalysis of cyclohexene, at 400°C, at space velocity 0.094 min⁻¹

Catalyst	V%/g	%  /g	%  /g
Ni-AH	17.71	8.37	51.52
Ni-A/AH	4.88	3.04	0.23

From the analysis of the products of the catalytic conversion of cyclohexene on $\text{Ni-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ we suggest that the following processes may have taken place under our experimental conditions :



On plotting the experimental data on coordinates of Balandin's equation (Balandin 1969), linear relations were obtained which conform to Balandin's equation, but the values of the constants determined had no physical meaning, that's because Balandin's equation was derived for unimolecular heterogeneous catalytic reactions taking place on surfaces completely covered by adsorbed molecules.

According to Ezzo (Ezzo *et al.* 1981, 1984) if the reaction takes place on the catalyst surface completely covered by the adsorbed molecules, and the rate determining step is one of the rates of surface reaction, the reaction may not proceed through the formation of a monomolecular catalytic complex but through the formation of a polymolecular catalytic complex intermediate, which depends on the nature of the catalyst and on the kinetic conditions.

The polymolecular mechanism accounts also for the increase in the weight of the catalyst after the experiments and for the disorder of the stoichiometry of the reaction.

All the results obtained can be explained by the formation of a polymolecular catalytic complex intermediate whose decomposition and desorption are considered as one kinetic stage which is the rate determining step.

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دراسة على التحول الحفزي غير المتجانس للألكانات الحلقية على حفاز النيكل ألومينا المحمل على ألفا - ألومينا ٢ - العملية الحفزية لتحول الهكسان الحلقي

هاله سليمان مظهر و سوزان أحمد علي

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مصر الجديدة - القاهرة - ص. ب. : ١١٧٥٧ - مصر

قامت عدة دراسات على تأثير المحمل على الحفازات من حيث الخواص الفيزيائية لسطوح الحفاز وعلى نشاطيته واختياريته، مما يدل على أهمية هذا التأثير.

وقد قمنا بتحضير حفاز النيكل ألومينا المحمل على ألفا - ألومينا (١, ٣١ ٪ من النيكل بالوزن) بواسطة التشبع لحبيبات الألفا - ألومينا بمحلول يحتوي على نترات النيكل والألومنيوم حسب السعة الأمتزازية للألومينا وتم استخدامه في دراسة سابقة لكيينيكية التحول الحفزي غير المتجانس للهكسان الحلقي على حفاز النيكل ألومينا المحمل على ألفا - ألومينا باستخدام النظام المستمر تحت الضغط العادي. واقترحت ميكانيكية التفاعل متعدد الجزئيات، ووجد تحسن في نشاطية الحفاز عند تحميل النيكل ألومينا على الألفا - ألومينا.

وفي هذه الدراسة تمت دراسة لكيينيكية التحول الحفزي غير المتجانس للهكسين الحلقي على نفس الحفاز وتحت نفس الظروف.

وأظهرت هذه الدراسة الرتبة الصفرية للتفاعل. وكانت النواتج الغازية، كما حددها التحليل الكروماتوجرافي، هي الميثان والهيدروجين، والنواتج السائلة هي الهكسان الحلقي والبنزين.

وأمكن حساب طاقة التنشيط الظاهرية وكانت قيمتها ١٨,٤ كيلوسعر/مول، ولا تعتمد على السرعة الفراغية، ولا تتأثر بفترة استخدام الحفاز ولا بظروف معالجته.

ولدراسة تأثير ظروف المعالجة للحفاز السابقة للتفاعل على نشاطيته واختياريته تمت المقارنة بين نتائج عملية التحول على الحفاز المعالج بالهواء والحفاز المعالج بالهيدروجين عند أقل وأعلى درجة للحرارة أجريت عندها التجارب، وقد أعطى الحفاز المعالج بالهيدروجين نشاطية أكثر في معظم الأحيان.

وبمقارنة النتائج التي تم الحصول عليها في هذه الدراسة بنتائج دراسة سابقة لتحول الهكسين الحلقي على حفاز النيكل ألومينا، وجد أن تحميل النيكل ألومينا على الألفا - ألومينا لم يؤد لتحسن في نشاطية واختيارية الحفاز في عملية تحول الهكسين الحلقي. وقد أرجع هذا لكبر كمية النواتج المتكثفة على سطح حفاز النيكل ألومينا المحمل على ألفا - ألومينا مما يؤدي إلى خفض نشاطيته في عملية تحول الهكسين الحلقي.

وقد اقترحت ميكانيكية التفاعل متعدد الجزيئات للتفاعل.