Proc. Indian Acad. Sci., Vol. 86A, No. 1, July 1977, pp. 65-79. © Printed in India.

Reactions of ketones on oxide surfaces. I. Reaction sequence of cyclohexanone on alumina

P GANGULY*
Department of Chemistry, Loyola College, Madras 600034
* Present Address: Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012

MS received 14 April 1977

Abstract. The reaction of cyclohexanone on alumina is investigated at various temperatures and contact times. The poisoning of the surface of pure alumina as well as of alumina impregnated with different amounts of sodium is also studied. The main reaction products are a dimeric aldol condensation product and cyclohexene. The reaction sequence of cyclohexanone on alumina involves first a rapid polymerisation of cyclohexanone on the surface. At low temperatures, hydrogen transfer from the polymer to cyclohexanone is responsible for the formation of cyclohexene, the polymer itself being converted to coke which poisons the surface. At higher temperatures the disproportionation of cyclohexanone is the dominant mechanism for the formation of cyclohexene. Cyclohexanol itself is not formed under the reaction conditions employed. Conditions of low acidity and temperature favour the formation of the dimer.

Keywords. Heterogeneous catalysis; alumina catalysis; transformation of cyclohexanone.

1. Introduction

The use of alumina as a catalyst for several reactions such as the dehydration of alcohols, isomerisation of olefins, cracking of hydrocarbons, etc., or as support for metal or metal oxide catalysts is well known. The nature of the active sites on alumina for such reactions are generally considered to be acid sites which could be Lewis acids or bronsted acid. The role of the basic sites on the surface such as the oxide ions or the hydroxide ions in the catalytic activity of alumina has been little studied in spite of the fact that these ions constitute physically a very large part of the surface. Quite some time back the basic sites have been postulated to be necessary for various processes such as the adsorption of alcohols (Greenler 1962; Arai *et al* 1968; Knozinger 1968; Jain and Pillai 1967), or for adsorption of ethylene and acetylene (Yates and Lucchesi 1961; 1963). Since then very little work has been done to investigate further the role of the basic sites. Hightower and Hall (1970) have showed that the oxide ions have a role to play in the isomerisation of olefins, while Rosynek *et al* (1975 and 1976) have found that the highly energetic oxide ions responsible for the formation of a carbonate structure with carbon dioxide are also responsible for the deuterium exchange reactions. The lack of interest in the role of the oxide ion is perhaps because their basicities would be determined anyway by the strength of the acid sites neighbouring them, as reflected in the dual acid-base sites proposed by Peri (1965). Thus recently, Szabo and Jover (1973) have studied the influence of the surface basicities of η-, γ-, and α-aluminas on the dehydration of alcohols. They have found that a two-centre mechanism involving an acidic and a basic site is probably the correct one. Gerberich *et al* (1966) have proposed that the dual acid-base site responsible for the formation of NH_2^- during the adsorption of ammonia on alumina (Peri 1965) is also responsible for the isomerisation of olefins. The importance of a basic site is evident from the need of such a site to abstract a proton from NH_3 to give NH_2^-, although it may be the adsorption on a strong neighbouring site that facilitates the abstraction of the proton. A better idea of the role of basic sites could be obtained if a study is made of a facile base-catalysed reaction such as the aldol condensation of ketones.

The aldol condensation reactions in the vapour phase over silica catalysts have been studied extensively by Malinowski *et al* (1963, 1964a, 1964b). They have used mainly aldehydes to investigate the aldol condensation reaction. Aldol condensation reactions of ketones over alumina has been briefly investigated by Scheidt (1964). Ketones are also reported to be transformed to olefins over alumina. Blouri and Ahmadi (1969) have investigated the reaction of straight-chain ketones over two alumina catalysts and have found that the formation of olefins is greater over the more acidic catalysts. Piehl (1969) has also reported the formation of olefins from aldehydes and ketones over MnO_2–Al_2O_3 catalysts in the presence of nitrogen. It seems therefore, that by studying the behaviour of metal oxide catalysts towards both the aldol condensation and olefin-forming reactions one could arrive at some conclusions regarding the importance of the basic sites vis-a-vis the acidic sites. No such systematic work seems to have been carried out so far.

We report in this and a subsequent paper the results of our study on the vapour phase transformation of cyclohexanone over alumina catalysts. The choice of cyclohexanone has been dictated by the fact that the simpler straight-chain ketones give rise to complicating side reactions such as fragmentation and skeletal isomerisation (Blouri and Ahmadi 1969; Cockern and Fry 1967; Newton and Coburn 1942; Jagannathan 1968). In this paper an attempt has been made to elucidate the reaction sequence by studying the product distribution at various time intervals during a reaction in order to study the poisoning of the catalyst, and also by studying the effect of various flow rates. In a subsequent paper we shall deal in more detail with the actual involvement of the active sites by studying the influence of various selective poisoning agents on the reaction.

2. Experimental Methods

2.1. *Apparatus*

The flow system used for the catalytic reactions had a slanting reactor with a static catalyst bed, and is similar to the flow system described by Upreti *et al* (1963). 2 g of dry catalyst was packed between layers of glass wool. A thermocouple measured and also controlled the temperature of the catalyst bed. The size of the catalyst particles was between 40 and 60 mesh. The catalysts were activated and regenerated by heating in air at 500°C. An ice-salt freezing mixture condensed the catalysate which was collected and analysed gas-chromatographically after removal of water. Nitrogen (partial pressure = 0.1 atm.) was used as a carrier gas. Before the start of the reaction the apparatus was flushed with dry nitrogen for about two hours. The results in the presence of air was the same as that in the presence of nitrogen.

Ammonia adsorption studies on alumina and some sodium-impregnated alumina were carried out in a conventional BET type of apparatus. The catalysts were evacuated at 500°C to 10^{-5} mm Hg before the introduction of ammonia.

Partial pressure studies with water was carried out with a slight modification of the apparatus. Water, as steam,was passed along with nitrogen just after cyclohexanone was introduced into the reactor.

2.2. *Analysis*

The liquid products of the catalysate of some trial runs carried out under various conditions over the alumina catalysts were collected and fractionally distilled in a Podbielniak distillation column. The high-boiling compounds were fractionally distilled under reduced pressure. The various fractions were tested for purity gas-chromatographically and identified by IR.

The various chromatography columns that were used are a 2-meter column of Carbowax-200 (20%) supported on chromosorb, a 2-metre column of 15% Bentone-34 and 10% Apiezon-L mixture supported on firebrick, and a five-metre SE-30 column. Hydrogen was used as the carrier gas.

2.3. *Materials*

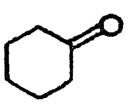
Cyclohexanone was purified by distillation to give more than 99.9% purity as determined gas-chromatographically and spectroscopically. The nitrogen used as the carrier gas was stated to be more than 99% pure. It was further purified by passing the gas over metallic copper turnings kept at 800°C and then dried in two silica-gel drying towers.

Alumina-*A* was prepared by the hydrolysis of freshly distilled aluminium isopropoxide (200g) in doubly distilled water (2 litres). The precipitate was washed several times with doubly distilled water and then allowed to stand for three days under doubly distilled water. The precipatate was then filtered and dried at 110°C for 72 hr. The dried hydrate was powdered and sieved to get particle sizes between 40 and 60 mesh and then activated by heating in air at 500°C for 24 hr.

Alumina-*AA* was another batch of catalyst prepared by the same method. This batch was used for impregnating with sodium. The impregnation of sodium was carried out with sodium carbonate solution (5N). After impregnation the catalysts were heated to 500°C for 24 hr. Four sodium-impregnated catalysts were thus prepared containing approximately 0·5, 1·0, 2·0, and 3·0 wt.% sodium. These catalysts were designated as alumina -*AA*0.5Na, -*AA*1.0Na, -*AA*2.0Na and -*AA*3.0Na, respectively.

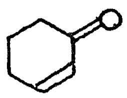
3. Results

The transformation of cyclohexanone (I) over alumina gives several products especially at high contact times and at high temperatures. The compounds identified as the major components of the products are cyclohexene (II), a dimer 2-(1-cyclohexen-1-yl) cyclohexanone (III), and phenol (IV). Another compound obtained under conditions of cyclohexene formation has been identified as cyclohex-1-en-3-one (V) (Forest Woods 1962) although it could not be distilled from the product in a pure state. 2-Cyclohexylidencyclohexanone (VI) did not seem to be formed. Cyclohexanol (VII) could not be obtained in the product of any experiment including those employing heavily sodium-impregnated catalysts. Similarly neither benzene nor cyclohexadiene could be detected. These compounds are formed during the dehydration of cyclohexenols (which are double bond isomers of the enolic form of cyclohexanone) over alumina (Pines and Manassen 1965). Forest Woods (1962) has also reported the formation of cyclohexadiene and benzene among other products during the reaction of cyclohexanone over alumina. Other authors (Adkins and Watkins 1951; Nazarov *et al* 1952, Guseva 1947) who have studied the transformations of cyclohexanone over alumina, however, do not report the formation of cyclohexadiene or benzene. Some methylcyclopentenes were formed at high contact times and high temperatures, obviously due to the isomerisation of cyclohexene.

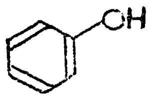


I

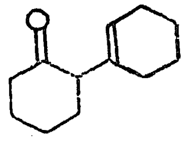
II



III



IV



V

Bartlett and Woods (1940) have reported the vapour phase dehydration of 2-hydroxycyclohexanone over alumina to cyclohex-1-en-3-one (henceforth referred to as cyclohexenone) and they have observed the disproportionation of this compound to cyclohexanone and phenol. The exclusive formation of 2-(1-cyclohexen-1-yl) cyclohexanone (henceforth referred to as the dimer) over alumina catalysts has been reported by Scheidt (1964). At high contact times and temperatures some compounds with retention times similar to those of biphenyls and hydrogenated biphenyls (henceforth referred to as biphenyls) were obtained. The biphenyls and the polymeric products were commonly classified as polymers for convenience in the tables. Gas evolution was negligible and no analysis of the gaseous products was carried out.

3.1. *Changes in the composition of the catalysate with time*

Most investigators, working with carbonyl compounds, have found a rapid poisoning of the catalyst surface during the reaction (Blouri and Ahmadi 1969; Pines and Manassen 1965). In order to understand this poisoning better we have studied the change in the composition of the catalysate with time. The temperature chosen was 400°C, the condition under which the reaction of cyclohexanone over alumina has been studied by other workers (Forest Woods 1962; Adkins and Watkins 1951; Nazarov *et al* 1952; Guseva 1947). Cuts at every ten minute interval, starting from the fifth minute, were collected during an experiment lasting an hour and estimated gas-chromatographically.

In the tables and figures that follow, the products were estimated in terms of the mole percent of cyclohexanone reacting to form them. The methylcyclopentenes when formed were included in the value for cyclohexene. It has been assumed that the weight percent polymer in the products is equivalent to the mole per cent of cyclohexanone reacting to form the polymer. When the concentration of biphenyls in the polymer is high it is indicated by an asterisk.

The formation of cyclohexene by a disproportionation reaction of cyclohexanone mentioned by the earlier workers mentioned above may be written as follows:

$$\begin{aligned} &2 \text{ cyclohexanone} \rightarrow \text{cyclohexenone} + \text{cyclohexene} + \text{water} \\ &2 \text{ cyclohexenone} \rightarrow \text{cyclohexanone} + \text{phenol}. \end{aligned} \tag{1}$$

From reaction (1) it can be seen that the formation of 1 mole of phenol gives rise to the formation of 2 moles of cyclohexene, while for each mole of cyclohexenone in the product one mole of cyclohexene is formed. A factor ϕ defined as

$$\phi = \frac{\text{mole per cent of cyclohexene}}{2(\text{mole per cent of phenol}) + \text{mole per cent of cyclohexenone}}$$

gives therefore a measure of the disproportionation reaction (1).

Table 1 gives the composition of the catalysate at various time intervals and various contact times over alumina-*A*. The contact time is expressed in hours as the reciprocal

Table 1. Composition of catalysate at various time intervals

WHSV^{-1} hr.	Time mins	Cyclohexanone wt. %	Products. (Mole% of cyclohexanone reacted)					ϕ
			Cyclohexene	Phenol	Cyclohexenone	Dimer	Polymer	
0·016	5	82·1	72·6	8·0	2·5	2·3	14·6	3·93
	15	87·2	67·6	12·1	3·9	3·2	13·3	2·41
	25	90·6	63·8	13·8	4·6	3·5	14·3	1·99
	35	90·4	60·9	14·5	5·0	3·2	16·4	1·74
	45	91·6	61·7	15·4	5·1	4·5	13·3	1·72
	55	92·4	59·7	15·1	5·5	5·4	14·2	1·67
0·020	5	37·6	81·4	11·6	2·7	..	4·3	3·14
	15	53·0	75·0	15·6	3·8	..	5·6	2·14
	25	66·2	72·7	17·8	4·6	..	4·9	1·81
	35	74·6	69·2	18·9	4·5	1·2	6·2	1·64
	45	76·2	70·0	18·3	4·5	3·6	3·6	1·70
	55	79·0	69·7	18·3	4·7	3·5	3·8	1·62
0·029	5	31·8	66·5	16·2	3·0	..	14·3*	1·88
	15	44·0	59·9	21·5	4·4	..	14·2*	1·26
	25	55·4	60·2	23·3	4·4	..	12·1*	1·18
	35	63·8	56·3	22·9	4·6	..	16·2*	1·12
	45	66·9	59·4	24·8	4·6	..	11·2*	1·09
	55	69·2	57·7	23·4	4·6	..	14·3*	1·12
0·047	5	27·0	53·5	24·2	3·9	..	18·4*	1·03
	15	32·4	51·2	26·0	4·0	..	18·8*	0·91
	25	37·3	51·7	26·7	4·2	..	17·4*	0·90
	35	39·8	51·3	28·4	4·1	..	16·2*	0·84
	45	40·2	50·0	27·2	3·9	..	18·9*	0·86
	55	40·5	50·2	27·4	4·1	..	18·3*	0·85

Catalyst : Alumina-A; Temperature: 405 ± 2°C;
*Considerable amount of biphenyls in the polymer.

of the weight hourly space velocity ($WHSV^{-1}$). It can be seen from the table that at all contact times there is a rapid poisoning of the activity of the catalyst, judging by the per cent of cyclohexanone undergoing conversion. At the end of these experiments the catalysts were black in colour due to the formation of coke. The extent of conversion of cyclohexanone to cyclohexene decreases with time while that to the dimer increases. The value of ϕ decreases with time as well as with contact time (figure 1). The high value of the factor ϕ (greater than 1) at the initial period of each experiment, especially at low contact times, suggests that at this stage cyclohexene is obtained by a mechanism other than the disproportionation reaction (1).

In figure 2 and table 2, the results of similar experiments carried out with sodium-impregnated alumina catalysts at 250°C are given. It is well known that sodium impregnation poisons the acid sites of alumina (Pines and Haag 1961). It can be seen from figure 2 that with increasing sodium-content of the catalyst the rate of poisoning decreases, till for the 3 % sodium-impregnated catalyst there is no poisoning at all. The colour of the alumina-*AA* catalyst was dark brown after the experiment, while for the alumina-*AA*0.5Na catalyst it was light brown, for the alumina-*AA*1.0Na catalyst it was yellow, and for the alumina-*AA*3.0 Na catalyst it was white. This shows decreasing amount of coke formation with increasing sodium content. The factor ϕ is very high in the cases where cyclohexenone or phenol was formed. That acid sites are responsible for the formation of cyclohexene is seen from the fact that with the 1 % sodium-impregnated catalyst only traces of cyclohexene is obtained and that only in the initial stages.

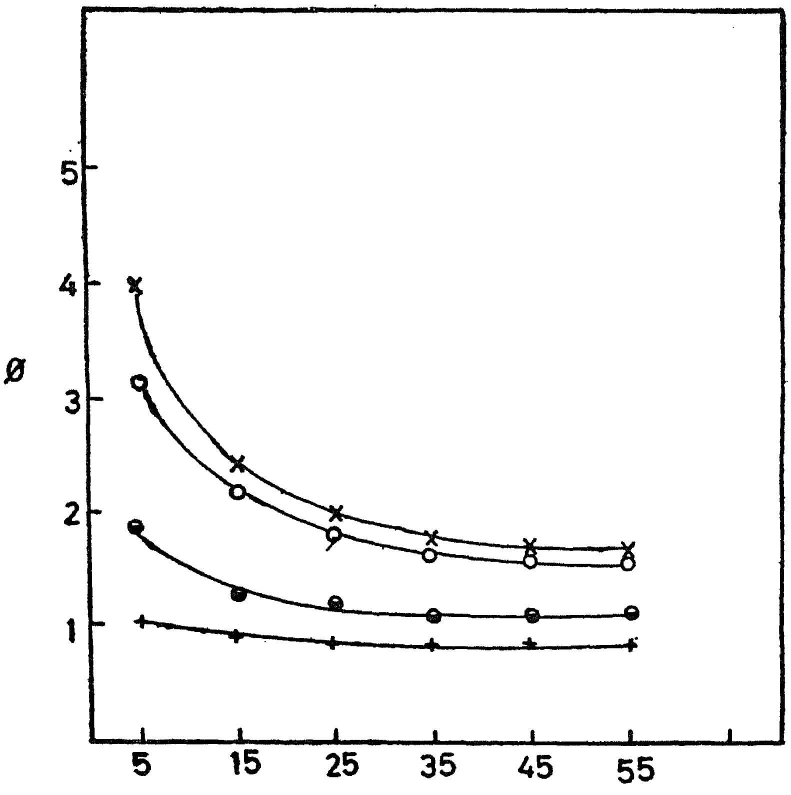


Figure 1. Change in the factor ϕ with time. Catalyst: Alumina-*A*; Temperature: 405±2°C; $WHSV^{-1}$: × =0·016, O=0·020, ◒ =0·029; + =0·047.

Table 2. Composition of catalysate at various time intervals

Catalyst	Time mins	Cyclohexanone wt. %	Products. (Mole % of cyclohexanone reacted)		
			Cyclohexene	Dimer	Polymer
Alumina-*AA*	5	78·4	56·0	23·4	20·6
	20	88·7	35·6	36·7	27·7
	35	97·3	25·9	48·9	26·0
	50	98·6	11·0	51·0	38·0
Alumina-*AA*0.5Na	5	76·1	10·8	76·3	12·9
	20	86·7	4·2	81·0	14·8
	35	89·8	traces	85·3	14·7
	50	92·3	..	88·0	12·0
Alimina-*AA*1.0Na	5	70·6	1·4	84·2	14·4
	20	72·4	..	86·1	13·9
	35	82·1	..	87·4	12·6
	50	86·5	..	91·0	9·0
Alumina-*AA*3.0Na	5	70·1	..	87·0	13·0
	20	64·7	..	86·8	13·2
	35	70·6	..	88·4	11·6
	50	70·3	..	92·3	7·7

WHSV^{-1}= 0·093 hr.; Temperature=250±2°C.; cyclohexenone and phenol not formed at this temperature.

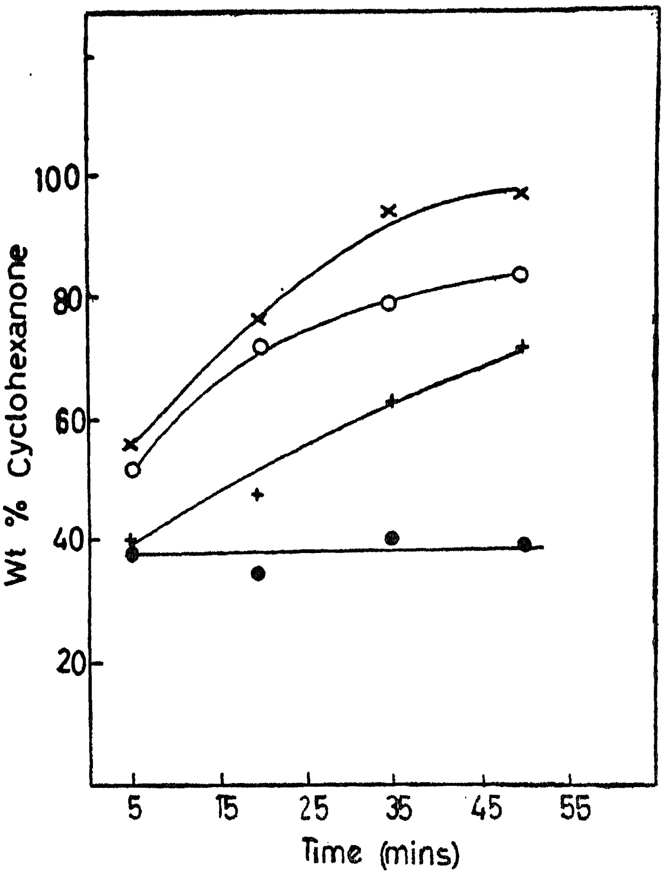


Figure 2. Change in activity of sodium-impregnated catalysts with time. Temperature: 250±2°C; Catalysts: × =Alumina -*AA*, O=Alumina-*AA*0.5Na, + =Alumina-*AA*1.0Na, ● =Alumina-*AA*3.0Na.

3.2. *Influence of contact time*

In figure 3 the effect of contact time on the product distribution during the reaction of cyclohexanone over alumina-*A* catalyst at 250°C is shown. Under these conditions cyclohexenone and phenol are formed. The contact times chosen were those for which the mass balance and conversion were reasonable. As we are interested in the influence of the catalyst during the early stages of the reaction, the catalysate obtained in the first half-hour of the experiment was collected and analysed. Nitrogen was passed during the experiments as a carrier gas at a partial pressure of 0.1 atm.

It can be seen from figure 3 that at low contact times the percentages of polymer in the products are rather high. With increase in contact time the percentage of polymer in the product decreases and goes through a minimum. At high contact times the increase in the polymer concentration is mainly due to the presence of biphenyls. Both cyclohexene and the dimer go through a maxima with increasing contact time.

In figure 4 the results of contact time studies at 345°C over alumina-*A* are given. At this temperature cyclohexenone and phenol are formed. It can be seen from the figure that there is a maximum in the concentration of cyclohexene in the products, similar to that observed at low temperatures (figure 3). The maximum in the case of the dimer comes at still lower contact times. In the case of cyclohexene, however, there is an increase in its concentration in the products with increasing contact time after the maximum is reached. This increase parallels the increase in the concentration of phenol in the products. This strongly indicates that at high contact times

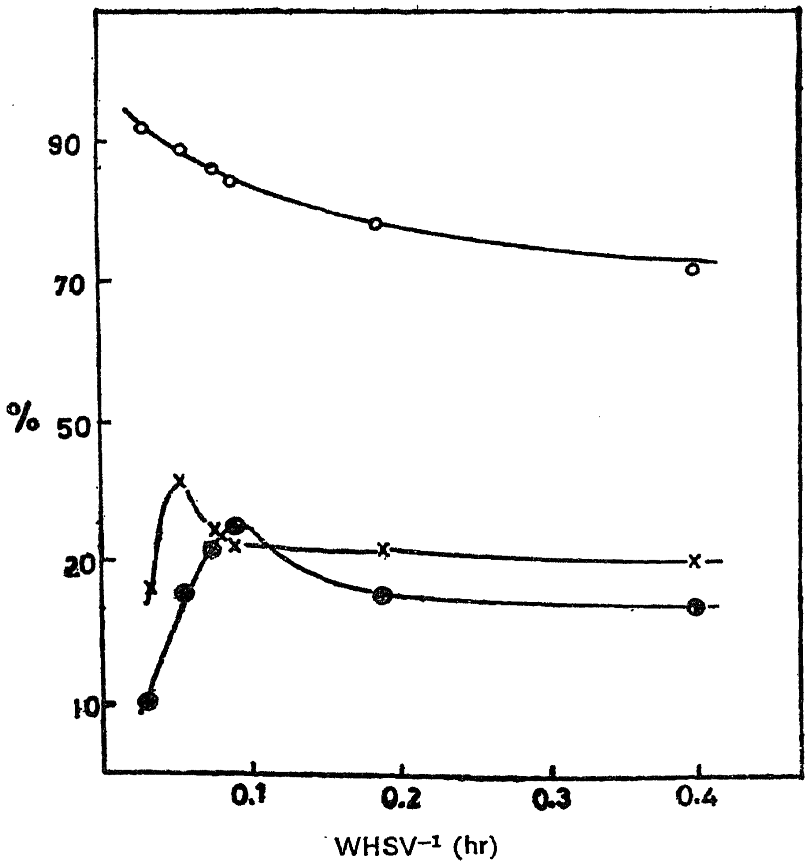


Figure 3. Influence of contact time. Catalyst: Alumina-*A*; Temperature: 253±2°C; O = weight per cent cyclohexanone in the catalysate; × = cyclohexene and ⊗ = dimer (mole %) in the catalysate.

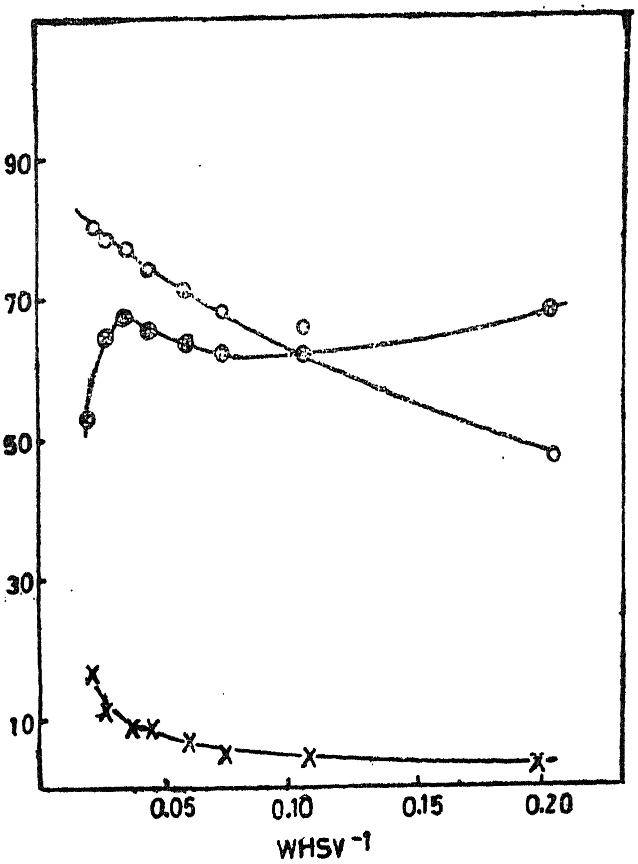


Figure 4. Influence of contact time. Catalyst: Alumina-*A*; Temperature: 342±2°C. O=cyclohexanone (wt. %); ⊗=cyclohexene (mole %) and × =dimer (mole %) of cyclohexanone reacted.

reaction (1) becomes dominant. The concentration of cyclohexenone goes through a maximum with increasing contact time showing that it is an intermediate in the formation of phenol.

3.3. *Adsorption of ammonia*

The results of the ammonia adsorption studies at various pressures at room temperature, and at various temperatures at 400 mm Hg pressure is given in figure 5. The high pressure of ammonia was chosen so that weak acid sites could be distinguished. It is seen that even with the heavily sodium-impregnated catalysts some ammonia is retained on the surface at rather high temperatures. The ammonia adsorption capacity, however, decreases with increasing temperature and with increasing sodium content.

3.4. *Influence of water vapour*

The results on the influence of water vapour on the reaction of cyclohexanone is shown in figure 6. The results are compared with those in the presence of nitrogen. Water vapour does not change significantly the extent of conversion of cyclohexanone over alumina catalysts. At low partial pressures the formation of cyclohexene is reduced, while at the higher partial pressures the formation of the dimer is reduced.

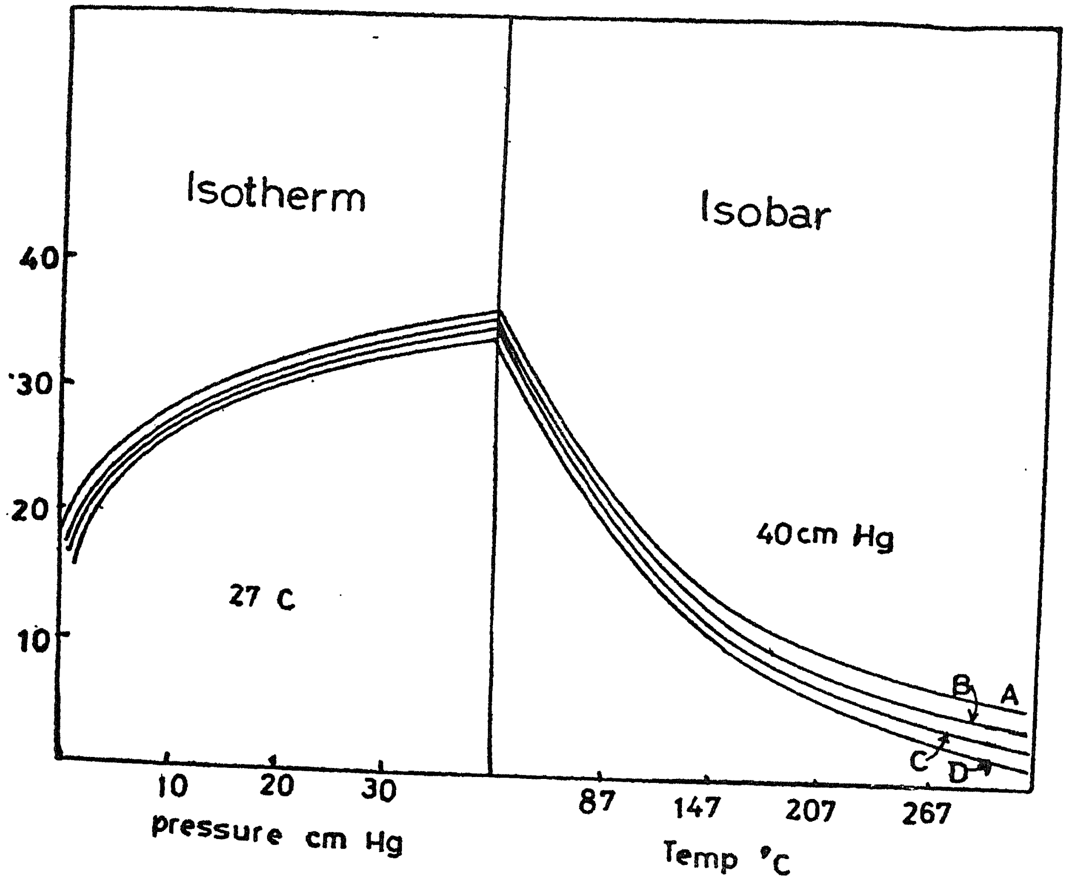


Figure 5. Adsorption of ammonia on sodium-impregnated alumina-*AA* catalysts. Curve A = Alumina-*AA*, B = Alumina-*AA*0.5Na, C = Alumina-*AA*0.0Na, D = Alumina-*AA*2.0Na.

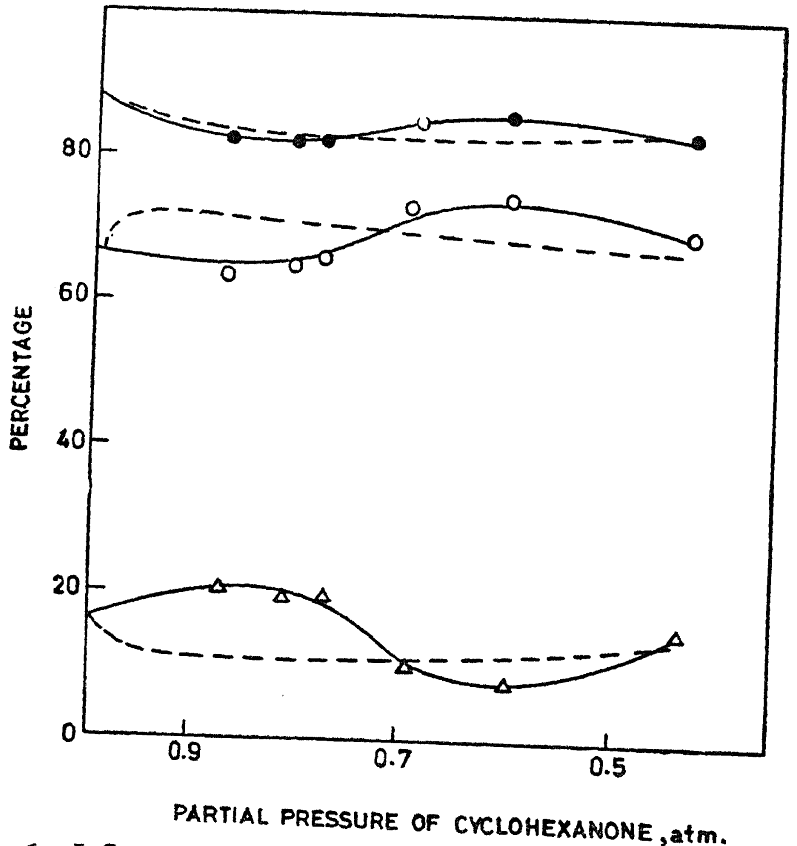


Figure 6. Influence of partial pressure of water. — =in presence of nitrogen, ---- =in presence of water. Catalyst: Alumina-*A*; Temperature: 320±2°C; ● =cyclohexanone (wt %); O= cyclohexene and △ =dimer (mole % of cyclohexanone reacted).

4. Discussion

As is seen from the above results the reaction of cyclohexanone over alumina is rather complicated. Nevertheless some conclusions can be drawn from the results on the change in the composition of the catalysate with time and with contact time which fit into a consistent picture for the reaction sequence.

4.1. *Change in the composition of the catalysate with time*

The high value of ϕ at the beginning of each run (figure 1, table 1) shows clearly that the disproportionation reaction (1) is not the only mechanism by which cyclohexene is formed. The dehydration of cyclohexanone to cyclohexadiene and its disproportionation to cyclohexene and benzene is certainly a possible pathway (Forest Woods 1962; Pines and Manassen 1965). But the failure to detect cyclohexadiene or benzene in our reaction products rules out this mechanism.

The presence of coke on the alumina catalysts at the end of each experiment shows that some dehydrogenation has taken place and it is likely that it is this " coking " process that is responsible for the formation of cyclohexene. In the initial stages cyclohexanone reacts to form a polymer on the surface, probably by a series of condensation reactions. Hydrogen transfer takes place from the polymer on the surface to an adsorbed cyclohexanone molecule to give ultimately cyclohexene, the polymer being itself transformed into coke in the process. The coke that is formed poisons the active sites on the surface of the catalyst and thereby decreases its activity. This is reflected in the decrease in the amount of cyclohexanone converted with increasing time (table 1). The reduced activity of the catalyst inhibits the condensation reaction of cyclohexanone from proceeding towards the polymeric stage, probably because the dimer, which is the first step of the condensation reaction is easily desorbed. The concentration of the dimer in the catalysate therefore increases with time as seen from table 1. As the hydrogen from the polymer gets exhausted, the only route for the formation of cyclohexene is by reaction (1), and hence the factor ϕ approaches unity with increasing time.

The factor ϕ approaches unity with increase in contact time also (figure 1). The fact that the disproportionation reaction (1) becomes increasingly favoured at high contact times shows that this reaction is much slower than the " coking " reaction. At high contact times, when less number of cyclohexanone molecules are available to the surface per unit time, coke may be formed by hydrogen transfer reactions taking place within the polymer itself. In a short time such an intrapolymer hydrogen transfer exhausts the hydrogen from the polymer available for transfer to cyclohexanone, and so reaction (1) again becomes the main pathway for the formation of cyclohexene at high contact times.

The results with the sodium-impregnated alumina catalysts also support the above view. Under the conditions studied, cyclohexenone and phenol are formed in very small amounts. That acid sites are responsible for the formation of cyclohexene is seen from the fact that no cyclohexene is formed over alumina-*AA*2.0Na catalyst. As mentioned earlier the colour of the alumina-*AA*3.0Na catalyst is white after the reaction showing the absence of any coke on the surface and hence of any poisoning. This is perhaps the reason why the alumina-*AA*3.0Na catalyst is the most active.

The acid sites on the 3% sodium-impregnated catalyst is so weak perhaps that even the intrapolymer hydrogen transfer is not possible.

There seems to be a slight discrepancy in the discussion given above. This is that the formation of cyclohexene by reaction (1) or by the coking process requires strong acid sites. But at high contact times the formation of cyclohexene by the " coking " process is poisoned, while reaction (1), i.e., the disproportionation reaction, is still able to proceed. One possibility is that the sites responsible for the polymerisation is different from that required for hydrogen transfer, and that it is the polymerisation sites that are poisoned by the formation of coke. Another possibility arises from the fact that the alumina catalysts have a large fraction of its surface area on the walls of micropores. Under the reaction conditions employed, these micropores are perhaps filled by the high-boiling compounds arising from the multiple condensation of cyclohexanone. These compounds are converted into coke in the pores and block the access of any reactant to the surface of their walls. The reaction of cyclohexanone then takes place on the relatively flat surfaces that are left unblocked. This favours the desorption of the intermediate dimer in the condensation reaction, and also the products of simultaneous disproportionation reaction (Wheeler 1958). Such a screening of the surface of the catalyst by higher condensation products have been postulated by Ivanov *et al* (1921) who have studied the condensation of acetaldehyde over various metal phosphate catalysts. They have found that the activity per unit surface area increased with increasing radius of the pores of the catalysts and did not depend on their chemical nature.

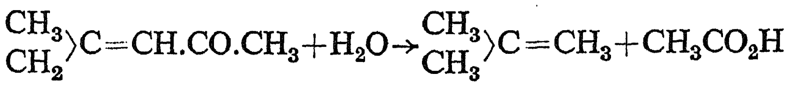
4.2. *Influence of contact time*

The results on the influence of contact time (figure 3) show that on a fresh alumina catalyst the first step is the condensation reaction which rapidly proceeds to the polymeric stage and rapidly covers the surface. At this stage the concentration of the polymer in the catalysate would be a minimum. It is this polymer on the surface that is responsible for the formation of cyclohexene by the " coking " process mentioned above. The maximum in the concentration of the dimer with increasing contact time is probably an artefact arising from the intrapolymer coking and consequent poisoning of the surface. It is for this reason perhaps that the maximum in the formation of cyclohexene is obtained, as there would not be sufficient hydrogen on the surface after the intrapolymer coking. The maximum in the concentration of the dimer may indicate that at high contact times it is converted into the biphenyls.

As mentioned earlier, at high temperatures (figure 4), the slow disproportionation reaction becomes important. Since sodium-impregnated catalysts poison the reaction giving cyclohexene, it is reasonable to assume that strong acid sites are responsible for the hydrogen transfer reaction. Probably a hydride ion transfer is involved (Tung and McInnich 1964). At low temperatures hydride ion abstraction by an acid site is possible only from molecules that are adsorbed for a long time on the surface and the polymer fulfils this condition ideally.

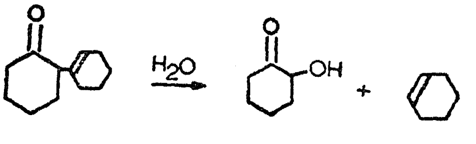
4.3. *Influence of water vapour*

The formation of isobutylene from acetone has been attributed (Demorest *et al* 1961; Midorikawe and Ito 1949) to an hydrolysis of the condensation product, mesityl oxide, giving at the same time acetic acid as shown in reaction (2):



$$\left.\begin{matrix}CH_3\\CH_2\end{matrix}\right\rangle C{=}CH.CO.CH_3+H_2O\rightarrow\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle C{=}CH_3+CH_3CO_2H \tag{2}$$

A similar process may also be operative with the condensation products of cyclohexanone. For instance, the condensation product 2-(1-cyclohexen-1-yl) cyclohexanone may undergo hydrolysis as shown in reaction (3) to give cyclohexene and 2-hydroxyxylohexanone which then undergoes dehydration to give cyclohexene and 2-hydroxyxylohexanone which then undergoes dehydration to give cyclohexenone (Bartlett and Woods 1940). Our studies (figure 6) show that water has little effect on the activity of the pure alumina catalyst for the conversion of cyclohexanone. At low partial pressures of water the per cent conversion of cyclohexanone to cyclohexene decreases while that to the dimer increases. At higher partial pressures the opposite happens, there being a slight decrease in the extent of conversion of cyclohexanone. These results may be interpreted in terms of the hydrolysis of the polymer on the surface at low partial pressures thus increasing the activity of the catalyst, and at high partial pressures the hydrolysis of the dimer itself. Although these results do not rule out conclusively reaction (3) as a pathway for the formation of cyclohexene and phenol, they certainly make reaction (3) unlikely.



4.4. *Reaction sequence*

From the above discussion a reaction sequence may be drawn up for the transformation of cyclohexanone over alumina, as shown below:

(a) cyclohexanone → dimer
(b) dimer → polymer
(c) polymer + cyclohexanone → cyclohexene + coke (4)
(d) cyclohexanone → cyclohexenone + cyclohexene
(e) cyclohexenone → cyclohexanone + phenol
(f) polymer → coke
(g) dimer → biphenyls

5. Conclusions

The aldol condensation of cyclohexanone giving the dimer as the first step (4a) in the reaction sequence does not seem to depend on the acidity of the catalyst. Malinowski *et al* (1963, 1964b, 1969), while investigating the aldol condensation reactions of aldehydes on silica catalysts, have attributed the improved activity of the sodium-impregnated alumina catalysts to the acidic-ONa group on the surface. Our studies on the adsorption of ammonia on the sodium-impregnated aluminas show that even the 3% sodium-impregnated alumina catalyst is capable of adsorbing a considerable amount of ammonia at rather elevated temperatures (figure 5). These studies show that some weak acid sites are present. The amount of ammonia adsorbed, however, decreased with increasing sodium content showing that sodium impregnation on alumina does not introduce any new weak acid sites. It seems likely, therefore, that a basic site—or a dual acid-base site with a stronger basic component—is sufficient for the aldol condensation to take place.

Miyata *et al* (1974) have found from their spectroscopic investigations on the adsorption of acetone on NiO and MgO, that the first step in the adsorption was the abstraction of a proton to form an enolate type of complex, the process taking place at rather low temperatures. This complex probably involves a dual acid-base site. The abstraction of a proton from an active methylene group has also been suggested for the ketonization of acids over alumina (Toshinobu *et al* 1974). The first step in the reaction of cyclohexanone is, therefore, also likely to be the abstraction of a proton from the active methylene group by a basic site to give a carbanion, or by a dual acid-base site to give an enolate type of complex.

The formation of an enolate type of complex on the adsorption of ketones on alumina is suggested by the almost exclusive formation of 2-(1-cyclohexen-1-yl) cyclohexanone in preference to the other possible dimer, i.e., 2-cyclohexylidenecyclohexanone. This kind of preference is also observed with other metal oxide catalysts (Swift and Bozik 1968; Badrian *et al* 1973). Perhaps the adsorbed form of the former is an enol which could be stabilised because of conjugation between the double bonds. Such an enol structure would not favour the abstraction of a proton from C_6 carbon atom that would be necessary for the polymerisation (by multiple condensation) to proceed. The dimer is therefore able to desorb. 2-Cyclohexylidenecyclohexanone, if formed, could undergo polymerisation easily as the abstraction of a proton from the other active methylene group is possible.

The exact mechanism of the reaction of cyclohexanone would be considered in more detail in a subsequent paper in which we will study the influence of temperature and the addition of various selective poisoning agents on the product distribution.

Acknowledgements

The author would like to express here his deep sense of gratitude to the late L M Yeddanapalli, who had suggested this problem and who passed away in the midst of this investigation. He also acknowledges the financial help given to him by the authorities of the Council of Scientific and Industrial Research, New Delhi.

References

Adkins H and Watkins S H 1951 *J. Am. Chem. Soc.* **73** 2184
Arai H, Saito Y and Yoneda Y 1968 *J. Catal.* **10** 128
Badrian A S *et al* 1973 *Neftekhimiya* **13** 733
Bartlett P D and Woods G F 1940 *J. Am. Chem. Soc.* **62** 2933
Blouri B and Ahmadi A 1969 *Bull. Soc. Chim. France* 171
Cockern W H and Fry A 1967 *J. Am. Chem. Soc.* **89** 5888
Demorest M, Mosberry D and Banforth J D 1961 *Ind. Eng. Chem.* **43** 2569
Forest Woods G 1962 *U.S. Dept. Com. Office Tech. Serv.* AD **278 110** 121 pp *Chem. Abst.* **60** 5381h

Gerberich H R, Lutinski F E and Hall W K 1966 *J. Catal.* **6** 209

Greenler R G 1962 *J. Chem. Phys.* **37** 2094

Guseva A N 1947 *Vestnik Moskov Univ.* 131; *Chem. Abst.* **42** 2733i

Hightower J W and Hall W K 1970 *Trans. Faraday Soc.* **66** 477

Ivanov V S *et al* 1961 Vestnik Leningrad Univ. **16** No. 22 *Sev. Fiz. i Khim.* 139; 1961 *Chem. Abst.* **56** 9465d

Jagannathan K 1968 Thesis University of Madras (Madras)

Jain J and Pillai C N 1967 *J. Catal.* **9** 322

Knozinger H 1968 *Angew. Chem.* (Int. Ed.) **7** 791

Malinowski S and Basinski S 1963 *Rocznicki Chem.* **37** 983

Malinowski S, Basinski S and Polanska B 1964 *Rocznicki Chem.* **38** 23

Malinowski S, Basinski S and Szezepanska S 1964 *Rocznicki Chem.* **38** 1361

Malinowski S, and Szczepanska S 1963 *J. Catal.* **2** 203; 1969 **15** 68

Midorikawa H and Ito M 1949 *Repts. Sci. Res. Inst.* **25** 32

Miyata H, Toda Y and Kubakowa Y 1974 *J. Catal.* **32** 155

Nazarov I N, Kotlyarveskii I L and Kuznetsov N V 1952 *Z. Obshchei Khim* **22** 1147

Newton L W and Coburn E R 1942 *Org. Syntheses* **22** 40

Peri J B 1965 *J. Phys. Chem.* **69** 211 220

Piehl D H 1969 *J. Chem. Soc.* **D 461**

Pines H and Manassen J 1964 1965 *Proc. Int. Cong. Catal.* Amsterdam I. p. 53

Pines H and Haag W O 1961 *J. Am. Chem. Soc.* **83** 2847

Rosynek M P 1975 *J. Phys. Chem.* **79** 1280

Rosynek M P and Strey F L 1976 *J. Catal.* **41** 312

Scheidt F M 1964 *J. Catal.* **3** 372

Swift H E and Bozik J E 1968 *J. Catal.* **12** 5

Szabo Z G and Jover B 1972 1973 *Catal Proc. Int. Cong.* ed Hightower J W (Amsterdam: North Holland) **1** 833

Toshinobu I, Adachi K, Okamoto Y and Teranishi S 1974 *Nippon Kagaku Kaishi* 862

Tung S E and McInnich J 1964 *J. Catal.* **3** 229

Upreti M C, Kuriacose J C and Sastri M V C 1963 *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **11** 651

Wheeler A 1958 in *Catalysis* ed P H Emmett (New York ;Reinhold) Vol II pp 105

Yates D J C and Lucchesi P J 1961 *J. Chem. Phys.* **35** 243

Yates D J C and Lucchesi P J 1963 *J. Phys. Chem.* **67** 1197