Reactions of ketones on oxide surfaces. II. Nature of the active sites of alumina

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Abstract. The nature of the active sites of alumina for the reaction of cyclohexanone was investigated by the introduction of selective poisoning agents both on the surface of the alumina as well as in the reactant itself. Thus additives which are basic in nature such as sodium ions, ammonia, pyridine, as well as acidic additives such as carbon dioxide, carbon monoxide, cyclohexanol, and isoproponal were used. Dual acid-base sites seem to be responsible for the catalytic properties. The sites responsible for the aldol condensation reaction giving a dimer seem to be similar to those sites responsible for the formation of ethers from alcohols, while the sites responsible for the formation of cyclohexene from cyclohexanone seem to be similar to those sites responsible for the formation of a carboxylate species on the adsorption of alcohols on alumina surfaces. A mechanism is proposed for the reaction of cyclohexanone which does involve the intermediacy of cyclohexanol to account for the formation of cyclohexene.

1. Introduction

In an earlier paper we had established the reaction sequence of a ketone such as cyclohexanone over alumina (Ganguly 1977). In the present paper we shall concern ourselves with the mechanism of the process and the nature of active sites involved. For this purpose we have selectively poisoned sites by either impregnation of the alumina with sodium or by adding impurities in the reactant. Such studies have been carried out earlier by several workers while studying the mechanism of the dehydration of alcohols over alumina catalysts. Thus Pines and Pillai (1961) have shown a poisoning influence of bases such as ammonia, triethyl amine, and piperidine on the dehydration of menthols. Ross and Bennet (1967) have observed that sodium impregnation poisons the dehydration activity. Jain and Pillai (1967) have proposed a carbonium ion mechanism on an acid site for olefin formation and an alkoxide ion mechanism on a basic site for ether formation. These conclusions were based on their studies in which they found that an acidic compound like phenol poisons the ether formation and a basic compound like pyri-

dine poisons the olefin formation.   In our studies we have studied the influence of sodium impregnation, the presence of several gases such as nitrogen, carbon monoxide carbon dioxide, ammonia, and the addition of impurities in the cyclohexanone such as pyridine, isopropanol, cyclohexanol on the reaction of cyclohexanone over alumina.

2. Experimental methods

2.1. *Materials*

Catalysts. The alumina-*AA* and the sodium-impregnated alumina catalysts alumina-*AA0.5Na* Alumina-*AA1.0Na*, Alumina-*AA2.0Na*, and Alumina-*AA3.0Na*, whose method of preparation is described in an earlier paper (Ganguly 1977), were used as catalysts.

Cyclohexanone and *nitrogen* were purified as mentioned in the earlier paper.   Spectroscopically pure cyclohexanone, isopropanol, pyridine, cyclohexanol, were used.

Cyclohexanol, isopropanol, and *pyridine* were separately distilled using a fractionating column and collected at their boiling points.   Distillation was carried out repeatedly till the compounds were gas-chromatographically and spectroscopically pure.   The purity of these compounds was checked before each experiment and redistilled if necessary.

Ammonia was prepared by adding a twenty per cent ammonia solution (AR, BDH) dropwise at a predetermined rate into a tower containing anhydrous powdered calcium oxide which was stirred continuously.   The calcium oxide removed the water and the ammonia gas was evolved at a steady rate.   The residual water in the ammonia gas was removed by passing through two towers containing calcium oxide.

Carbon monoxide was prepared by adding dropwise ninetyeight per cent formic acid solution at a predetermined rate into a stirred solution of pure sulphuric acid. The gas was passed through two washing towers, one containing NaOH solution and another containing water, and then through two drying towers containing silica gel.

Carbon dioxide was prepared using a Kipps apparatus with thirty per cent hydrochloric acid solution and marble chips.   The gas was passed through two saturated solutions of sodium bicarbonate and then through two towers containing solid sodium bicarbonate.

Procedure: Before each experiment the catalytic reactor described earlier was flushed with nitrogen gas.   Nitrogen at a partial pressure of 0·10 atm was always passed over the catalyst, during the reaction.   Gases such as hydrogen, carbon monoxide, carbon dioxide, ammonia were passed just after cyclohexanone was passed. The NH_3, CO and CO_2 production apparatus were flushed with the respective gases for 2 hr before they were passed into the reactor.   The miscible impurities such as cyclohexanol, isopropanol, and pyridine were mixed with cyclohexanone in the required proportions before being passed over the catalyst.

Analysis: The qualitative analysis of the products was done by fractional distillation of the products and by gas-chromatographic and spectroscopic identification of the distillate.   The quantitative analysis of the product was done by gas—chromatography as mentioned in Ganguly (1977).   When cyclohexanone was mixed with

liquids such as pyridine, cyclohexanol, and isopropanol, the product was analysed in terms of cyclohexanone reacted, excluding the possibility of the additives undergoing any reaction with cyclohexanone. In the case of isopropanol additives, small amounts of condensation products of acetone with cyclohexanone was obtained.

3. Results

As mentioned in Ganguly (1977) the main products of the reaction of cyclohexanone, (I), are cyclohexane (II), cyclohex-1-en-3-one (III), (referred to as cyclohexenone), phenol (IV), 2-(1-cyclohexen-1-yl) cyclohexanone (V) (referred to as dimer). Some other products were obtained in small amounts mainly as the end products of the reaction at high contact times and temperatures. These include some compounds with the same retention time such as the biphenyls and hydrogenated biphenyls. These and other products were included in the term "polymer".
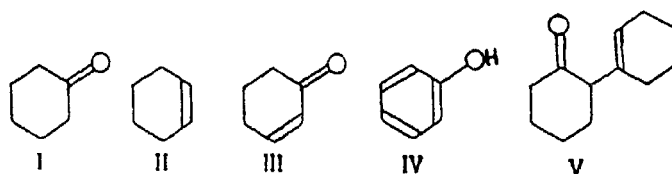

Table 1. Effect of temperature on activity of sodium-impregnated catalysts.[a]

Catalyst	Temp. °C wt. %	Cyclo- hexanone wt. %	Products. Mole % of cyclohexanone reacted.				
			cyclo- hexene	phenol	cyclo- hexenone	dimer	polymer
Alumina-*AA*0.5*Na*	254	85·7	—	—	—	91·5	8·5
	280	87·5	2·3	—	—	53·5	44·2
	309	89·7	12·4	—	—	47·1	40·5
	342	84·2	33·6	—	6·0	27·9	32·5
	388	74·9	54·3	3·4	11·2	16·1	15·0
Alumina-*AA*1.0*Na*	254	75·0	—	—	—	92·0	8·0
	280	77·8	—	—	—	83·1	16·9
	309	79·0	—	—	—	80·1	19·9
	342	82·5	4·3	—	—	74·8	20·9
	388	77·6	15·6	—	—	55·5	28·9
Alumina-*AA*2.0*Na*	254	72·1	—	—	—	88·1	11·9
	280	69·9	—	—	—	81·4	18·6
	309	70·5	—	—	—	89·4	10·6
	342	70·9	—	—	—	75·4	24·6
Alumina-*AA*3.0*Na*	254	70·8	—	—	—	86·4	13·6
	280	67·5	—	—	—	84·6	15·4
	308	65·1	—	—	—	81·3	18·7
	342	67·1	—	—	—	86·2	13·8
	388	70·2	—	—	—	85·1	14·9

[a] Feed = cyclohexanone, WHSV^{-1} = 0·061 hr. Nitrogen partial pressure = 0·1 atm

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The results of the activity of the sodium impregnated alumina-AA catalysts at various temperatures are given in table 1. Nitrogen at a partial pressure of 0·1 atm was passed along with cyclohexanone.

In table 2, the influence of sodium addition to the alumina-AA catalyst at 345°C is given. The nitrogen partial pressure was 0·45 atm. These results are compared in the same table with the results in the presence of other additives such as ammonia, pyridine, CO_2, CO, cyclohexanol and isopropanol at the same partial pressure of cyclohexanone (0·55 atm). The partial pressure of the additive was 0·35 atm and that of the carrier gas, nitrogen, was 0·1 atm.

Table 2. Effect of various additives on the activity of alumina and sodium-impregnated aluminas.[a]

Catalyst	Additive	Cyclo-hexanone wt. %	Products. Mole % of cyclohexanone reacted				
			cyclo-hexene	phenol	cyclo-hexenone	dimer	polymer
Alumina-AA	N_2	53·2	67·1	11·4	4·5	2·3	14·7
Alumina-AA0·5Na		76·0	48·4	0·8	3·4	28·0	19·4
Alumina-AA1·0Na		74·0	18·1	—	—	73·2	8·7
Alumina-AA2·0Na		61·6	—	—	—	88·0	12·0
Alumina-AA3·0Na		51·2	—	—	—	86·5	13·5
Alumina-AA	NH_3	51·2	63·8	12·1	7·2	8·4	8·5
Alumina-AA0·5Na		54·6	18·4	—	2·4	18·6	60·6
Alumina-AA1·0Na		54·2	7·2	—	—	46·5	46·3
Alumina-AA2·0Na		54·6	—	—	—	59·2	40·8
Alumina-AA	pyridine	66·1	71·2	9·4	6·0	6·2	7·2
Alumina-AA0·5Na		78·7	50·1	1·0	4·0	30·2	14·7
Alumina-AA1·0Na		76·2	19·1	—	—	80·1	0·8
Alumina-AA2·0Na		64·5	—	—	—	91·2	8·8
Alumina-AA3·0Na		59·0	—	—	—	98·2	1·8
Alumina-AA	CO_2	59·8	65·8	11·6	4·0	5·4	13·2
Alumina-AA0·5Na		74·0	44·2	11·2	3·2	28·4	23·0
Alumina-AA1·0Na		74·2	16·1	—	—	75·4	8·5
Alumina-AA2·0Na		74·0	—	—	—	85·2	14·8
Alumina-AA3·0Na		74·1	—	—	—	84·9	15·1
Alumina-AA	CO	54·2	68·6	10·9	5·5	2·1	12·9
Alumina-AA1·0Na		72·9	18·3	—	—	74·5	7·2
Alumina-AA3·0Na		52·9	—	—	—	85·1	14·9
Alumina-AA	Cyclo-hexanol	54·6	70·2	12·6	2·4	9·4	5·4
Alumina-AA0·5Na		55·2	1·6	1·61	3·2	31·4	10·6
Alumina-AA1·0Na		88·0	16·2	—	—	78·9	4·9
Alumina-AA2·0Na		91·3	—	—	—	94·3	5·7
Alumina-AA3·0Na		90·6	—	—	—	93·8	6·2

[a] Temperature: 345 ± 2°C; partial pressure of cyclohexanone = 0·55 atm., partial pressure of nitrogen = 0·1 atm (carrier gas); partial pressure of additive = 0·35 atm, flow rate = 0·088 mole/hr.
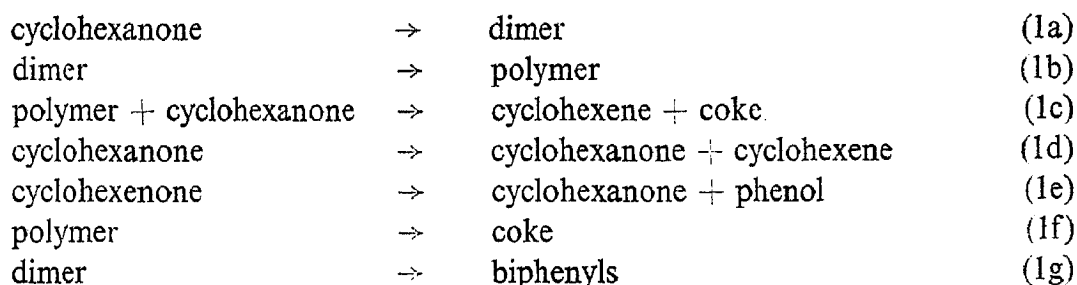
Table 3. Influence of isopropanol[a]

Catalyst	Mole % composition of the catalysate excluding polymer									
	cyclo-hexa-none	cyclo-hexene	phenol	cyclo-hexae-none	cyclo-hexa-none	dimer	acetone	isopro-panol	propy-lyne	Polymer wt. %
Alumina-*AA*	21·9	32·2	3·8	1·7	—	2·2	12·7	—	25·5	0·4
Alumina-*AA*0·5*Na*	21·6	31·3	0·3	1·7	—	6·1	25·7	—	13·2	0·7
Alumina-*AA*1·0*Na*	30·4	14·9	—	—	12·7	2·1	25·6	9·3	4·0	1·2
Alumina-*AA*2·0*Na*	31·1	—	—	—	26·7	4·5	25·0	10·3	1·4	2·3
Alumina-*AA*3·0*Na*	30·1	—	—	—	28·1	4·6	25·4	10·8	—	4·0

[a]Temp + 345 ± 2°C; Feed = cyclohexanone-isopropanol mixture in the molar ratio 55 : 35 with nitrogen as carrier gas at a partial pressure of 0·1 atm. Flow rate = 0·088 mole/hr/g.

The catalysate of the ammonia runs gave on shaking with hydrochloric acid a precipitate which was not found with the other runs. The reaction of carbonyl compounds such as cyclohexanone, acetaldehyde, crotonaldehyde, etc., with ammonia over alumina catalysts has been reported earlier (Chichibabin and Barkovsky 1941; Butler 1968). No attempt was made to identify the basic compounds, formed by the reaction of ammonia with cyclohexanone and these compounds were included in the weight per cent of cyclohexanone reacting to form the polymer.

4. Discussion

As discussed in the earlier paper (Ganguly, 1977), the reaction sequence for cyclohexanone on the alumina catalysts may be written as follows:

cyclohexanone	→	dimer	(1a)
dimer	→	polymer	(1b)
polymer + cyclohexanone	→	cyclohexene + coke	(1c)
cyclohexanone	→	cyclohexanone + cyclohexene	(1d)
cyclohexenone	→	cyclohexanone + phenol	(1e)
polymer	→	coke	(1f)
dimer	→	biphenyls	(1g)

At low temperatures and contact times (1c) is the main pathway for the formation of cyclohexene, while (1d) becomes important at high contact time and temperatures. The reactions (1f) and (1g) take place at high temperatures and high contact times.

The influence of various additives is discussed in terms of the influence of basic additives such as sodium ions, ammonia and pyridine which are expected to poison the basic sites, and weakly acidic additives such as carbon dioxide, cyclohexanol and isopropanol which are expected to poison the strong acid sites.
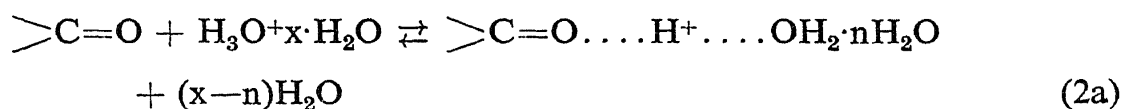
4.1. *Influence of bases : Influence of sodium*

It is seen immediately from tables 1 and 2 that the impregnation of sodium poisons the conversion of cyclohexanone to olefins but favours the formation of the condensation products. The formation of cyclohexenone and phenol is also poisoned by the addition of sodium ions. Our results are similar to the results of Ross and Bennett (1967) who have observed that sodium impregnation poisons the dehydration of alcohols to give olefins, and at the same time promotes the formation of ethers. Thus the sites responsible for the formation of olefins from alcohols and ketones and the sites responsible for the formation of ethers and condensation products from alcohol and ketone respectively seem to be the same.

Makarov and Shchekochikhin (1964) have found that impregnation with sodium ions prevents the formation of a carboxylate like species on the surface of alumina on the adsorption of ethanol. The sites responsible for the formation of these carbooxylate species have been associated with oxidative properties by Kagel (1967) who observed that hydrogen is evolved on the adsorption of ethanol on strongly acidic alumina. According to Kagel the alcohol is directly oxidised to the carboxylate species. Fink (1969), however, considers that the acetate or carboxylate structure is due to the oxidation of the alcohol group to a carbonyl group and the further saponification of the carbonyl group. A similar saponification mechanism has been proposed for the formation of a carboxylate-like species on the adsorption of acetone over metal oxides (Miyata *et al* 1974). Makarov and Shchekochikhin (1964) have suggested that the sites responsible for the formation of the carboxylate species are anion vacancies that get occupied on the addition of sodium ions. It seems likely, therefore, that these sites can abstract negative ions such as OH⁻ or H⁻ leaving a positively charges moiety which then loses a proton to give dehydration or dehydrogenation products of the original molecule.

It is seen from table 1 that, at low temperatures when cyclohexene formation is minimal, the activity of the sodium-impregnated alumina catalysts increases with the amount of sodium. As explained by Malinowski *et al* (1962, 1963, 1964), the more basic-ONa groups that are present on the surface may play an important part in improving the activity of the sodium-impregnated catalysts. At the same time the " coking " process (reaction (1c)), responsible for the formation of cyclohexene would reduce the activity of the more acidic catalysts. At high temperatures when cyclohexenone and phenol are formed (reactions (1d) and (1e)), the activity goes through a minimum with increasing sodium impregnation. This is seen better in table 2 where the results of the influence of sodium impregnation on the pure alumina-*AA* catalysts are given. The high activity of the pure alumina-*AA* catalysts is due to the formation of cyclohexene by the disproportionation reactions (1d) and (1e) With the addition of sodium ions the disproportionation reaction is poisoned and the activity decreases. With the heavily sodium-impregnated catalysts there is no poisoning due to " coking " and hence the 3% sodium-impregnated catalyst remains the most active.

As mentioned earlier, the ability to form cyclohexene is associated with those sites which have anion vacancies. At low temperatures the anion vacancies are occupied by the water formed during the reaction. At high temperatures the desorption of the water molecule becomes favoured and the anion vacancies become accessible to the reactants. Fripiat (1969) has proposed that the loosely bound oxygen ions on the

surface of alumina catalysts are the sites responsible for the strong acidic properties. Water is known to poison acid sites (Spannheimer and Knoezinger 1966) and acid-catalysed reactions (Gerberich and Hall 1966; Hall *et al* 1969). Pal'm *et al* (1962) have given the following mechanism for the protonation of carbonyl bases:

$$>C=O + H_3O^+x \cdot H_2O \rightleftarrows >C=O\ldots.H^+\ldots.OH_2 \cdot nH_2O$$

$$+ (x-n)H_2O \tag{2a}$$

$$>C=O\ldots.H^+\ldots.OH_2nH_2O \rightleftarrows >C^+-OH+(n+1)H_2O \tag{2b}$$

In this mechanism they have included the activity of water. In the presence of water the bonds in (2a) are formed with the bond strength being roughly that between hydrogen and covalent bonds. The $>C^+-OH$ bonds are formed only in the absence of any significant amount of water as in concentrated sulphuric acid. It is likely that over alumina catalysts, as the desorption of water from its surface increases with temperature, a mechanism similar to that given by reaction (2) would be operative. At high temperatures the formation of carbonium ions as in (2b) would favour the disproportionation reaction, the rate of hydrogen transfer being so fast that the " coking " process need not be the only process for the formation of cyclohexene.

4.2. Influence of ammonia

It is seen from table 2 that in the presence of ammonia, the conversion of cyclohexanone on the pure alumina catalyst is decreased while on the other catalyst it is increased. The per cent conversion of cyclohexanone to cyclohexene is decreased over all the catalysts. The colour of the alumina-*AA* catalyst was pale brown while after the corresponding experiment with nitrogen the colour of the catalyst was black. This showed that the " coking " process was poisoned in the presence of ammonia thus accounting for the decrease in the conversion to cyclohexene. Ammonia thus poisons the strong acid sites that are responsible for the formation of cyclohexene.

Over the sodium-impregnated catalysts there is a marked reduction in the per cent conversion of cyclohexanone to the dimer in the presence of ammonia, although there is an increase in the extent of reaction of cyclohexanone. One explanation is that the dimeric products may have reacted further with ammonia to give basic products. Another is that the condensation reaction may involve both acidic and basic sites. In the presence of ammonia the adsorption of cyclohexanone on the basic sites would be unhindered, but there would be a competition between the cyclohexanone and ammonia molecules for the acid sites. As a consequence, the amount of bimolecular condensation products would decrease. The extent of this decrease would be less with increasing sodium addition because the acid sites would have less of a role to play.

4.3. Influence of pyridine

It is seen from table 2, that there is a decrease in the total amount of conversion of cyclohexanone in the presence of pyridine. There is, however, an increase—if only

marginal—in the extent of conversion to cyclohexene and the dimer.   Pyridine does not seem to affect the primary products of the reaction.

The failure of pyridine to alter significantly the reaction of cyclohexanone is surprising as pyridine is known to poison Lewis acid sites (Parry 1967), and our studies with sodium-impregnated catalysts revealed that anion vacancies which should behave as Lewis acid sites are the likely sites responsible for the formation of cyclohexene. One reason may be that the adsorption of cyclohexanone on an acid site involves dual acid-base sites with the acid component being stronger.   Mohammed *et al* (1967) have shown that the basicity of carbonyl groups towards some Lewis acids may be much greater than their basicity towards protons, and may even be better than nitrogen containing compounds.   They have attributed this effect to the two lone-pairs of electrons on the oxygen atom of the carbonyl group compared to the single lone-pair of electrons on the nitrogen atom.   The extra lone-pair of the carbonyl oxygen is able to take part in the bonding with the Lewis acids through the unoccupied *d* orbitals of these acids.   Although the aluminium ion has no *d* orbitals, it is surrounded in alumina by hydroxyl groups (Peri 1965) in which the protons are slightly acidic (Spannheimer and Knoezinger 1966).   These slightly acidic protons may participate also in the adsorption of the carbonyl group by forming a bond with the second lone-pair of electrons in the oxygen atom.   As a result the basicity of the carbonyl group may be greater than that of the pyridine molecule.   The simultaneous participation of both the aluminium ions and the protons of the—OH group is similar to the Lewis-Bronsted pair proposed by Hall *et al* (1964) for the silica-alumina catalysts.

It is interesting to note in this connection the similarity of our results and those obtained by other authors studying the dehydration of alcohols over alumina concerning the influence of ammonia and pyridine.   Thus Pines and Pillai (1961) have shown that the dehydration reaction of alcohols is poisoned by ammonia and other bases, while Beranek *et al* (1961) have reported that pyridine does not poison it. This discrepancy can be accounted for if it is assumed that a dual acid-base site is involved in the dehydration of alcohols.   It is this participation by a dual acid-base site that is responsible for the negative effect of pyridine.

4.4. *Nature of adsorption of cyclohexanone on acid sites*

From the above studies it is evident that the adsorption of cyclohexanone on a strong acid site involves a dual acid-base pair with the acid component being stronger. The dual acid-base site is most likely an —Al$^+$—OH group. The adsorption of cyclohexanone takes place on this site via the carbonyl oxygen on the —Al$^+$—OH group according to the simplified sequence given in figure 1a.
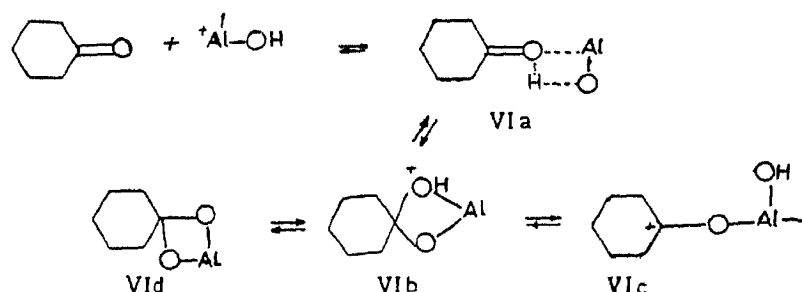

Figure 1a.   Adsorption of cyclohexanone on the acidic —Al —OH groups.

The species VId resembles the carboxylate species proposed by several authors for the adsorption of alcohols on strong acid sites (Kagel 1967; Fink 1969) and may be a precursor to it. It should be noted that the formation of the species VIa would be necessary perhaps at only low temperatures. At higher temperatures the species VIb, VIc, and VId could be formed straightaway.

4.5. *Influence of acids: Influence of carbon dioxide*

The adsorption of carbon dioxide on the surface of alumina has been studied by a number of authors (Fink 1969; Little and Amberg 1962; Parkins 1965; Peri 1966; van Cauwelaert and Hall 1972; Larson and Hall 1965; Saunders and Hightower 1970; Lunsford *et al* 1975; Rosynek 1975; Rosynek and Strey 1976). Carbon dioxide is known to poison the deuterium exchange sites and these sites have been associated with the interaction of energetic oxide ions with CO_2 to give CO_3^{2-} ions (Rosynek 1975; Rosynek and Strey 1976). Fink (1969) has suggested an interaction between carbon dioxide and —Al —OH groups on the surface to give a carbonate species. The participation of —Al —OH groups is similar to the mechanism proposed by us for the adsorption of carbonyl groups on the acid sites (figure 1a). According to Fink (1969), the most-basic —OH group would stabilise the carbonate structure the most. In this case the — ONa groups of the sodium-impregnated aluminas would stabilise the carbonate structure greatly, the sodium ions acting as weak acid sites. Malinowski and Szczepanska (1963) had attributed the adsorption of carbon dioxide on sodium-impregnated silica catalysts to the weak acid sites due to sodium. Since the aldol condensation reaction is poisoned by carbon dioxide, it is most likely that dual acid-base sites (with the basic component stronger) are responsible for the abstraction of a proton from the active methylene group to initiate the condensation reaction. The abstraction of a proton leaves a carbanion which may be attached to the aluminium ion constituting the weak acid site. Al—C bonds have been detected by a number of authors in infrared studies of various compounds adsorbed on alumina (Yates and Lucchesi 1961; 1963) (species VIIb; figure 1b). Another possibility is that an enolate structure (VIIc) is formed. The enolate structure has been observed in the infrared studies of adsorbed acetone molecules on oxide surfaces (Fink 1969; Miyata *et al* 1974). The enolate structure is expected to be quite stable. It is probably a mobile species on the surface of weakly acidic aluminas.
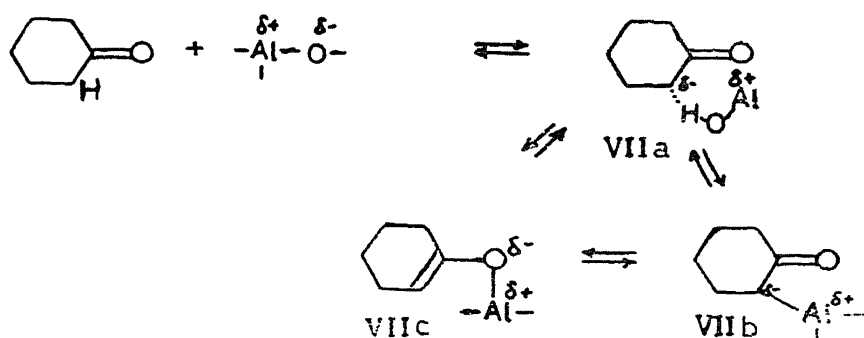
Figure 1b. Adsorption of cyclohexanone on the basic sites of alumina.

4.6. Influence of carbon monoxide

Carbon monoxide has no effect on the reaction of cyclohexanone. The adsorption of carbon monoxide on alumina has been found to be very weak and requires very strong acid sites to be adsorbed on the surface (Peri 1968; Amberg and Seanor 1965; O'Neill and Yates 1961; Borello *et al* 1971, 1974; Della-Gatta *et al* 1976). The extra stabilisation of carbon dioxide by the basic —OH groups as proposed by Fink (1969), does not appear to be present in the case of carbon monoxide. Carbon monoxide is therefore adsorbed on a single acid site and hence does not poison the reaction of cyclohexanone which requires dual acid-base sites.

4.7. Influence of cyclohexanol

It was seen earlier that the active sites involved in reactions of alcohols and ketones are similar. The active sites responsible for the formation of ethers from alcohols also seem to be the sites for the aldol condensation reaction. It is seen from table 2 that cyclohexanol poisons the activity of sodium-impregnated catalysts but does not affect the activity of the pure alumina-*AA* or the 0·5% sodium-impregnated alumina catalysts. The adsorption of alcohols on alumina give an alkoxide species (Greenler 1962; Triebman and Simon 1966; Arai *et al* 1968) which are thought to be intermediate in the formation of ethers (Topcheiva *et al* 1967; Knoezinger 1968). Kagel (1967) has suggested that the alkoxide species is formed when the —OH group of the alcohol molecule reacts with a surface oxide ion to give a surface hydroxide ion while the alkoxide moiety is coordinated to an acid site. Knoezinger *et al* (1968) have shown that basic compounds poison the ether formation while Jain and Pillai (1967) have shown that an acidic compound like phenol poisons the ether forming reaction. The possibility of dual acid-base sites being necessary for the formation of ethers from alcohols therefore arises again. Although the alkoxide species is not obtained over pure alumina catalysts from cyclohexanol (Rericha and Kochloeffl 1969) it may be stable over the sodium-impregnated catalysts. Secondary alcohols are known to give alkoxide species over metal oxide catalysts (Canerson and Blancher 1976). The poisoning of the condensation reaction observed on the sodium-impregnated catalysts in the presence of cyclohexanol could then mean that the dual acid-base sites responsible for the formation of ethers from alcohols are also responsible for the formation of the aldol condensation products from ketones. These sites should be similar to those poisoned by carbon dioxide.

The absence of any influence of both carbon dioxide and cyclohexanol on the more acidic catalyst indicates that the carbonyl group of cyclohexanone gets adsorbed on an acid site and the positive charge thus induced on the α-carbon atom makes the proton on the active methylene group more acidic than both cyclohexanol and carbon dioxide. On the more acidic catalysts, therefore, the adsorption of cyclohexanone would invlove a pair of dual acid-base sites in one of which the acid component is stronger while in the other the base component is stronger.

Since cyclohexanone is preferentially adsorbed on alumina compared to cyclohexanol, the presence of cyclohexanone should inhibit the dehydration of cyclohexanol. Vasserberg *et al* (1961) have found that in the presence of a ketone the dehydration of alcohol is poisoned. We find that under the temperature conditions and flow rates studied all the cyclohexanol underwent dehydration over the more acidic catalysts.

The acid sites required for the formation of cyclohexene from cyclohexanone may be stronger than those required for the dehydration of alcohols, and hence the isolation of cyclohexanol as an intermediate may not be possible as it would immediately be dehydrated to cyclohexene. Our studies with isopropanol show, however, that this may not be true.
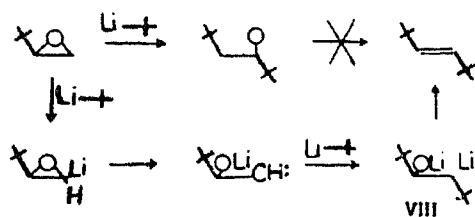
4.8. *Influence of isopropanol*

Isopropanol poisons the condensation reaction of cyclohexanone over the sodium-impregnated catalysts just like cyclohexanol. This confirms our abovementioned mechanism in which we have suggested that dual acid-base sites are involved.

An additional reaction is observed which is the hydrogen transfer reaction between the alcohol and the ketone. Such reactions have been reported by a number of authors on several catalysts (Miyanoto and Ogino 1976; Patterson and Burwell 1971; Schachter and Pines 1968; Friedlin *et al* 1968; Ramanna 1969). Kibby and Hall (1973), who have studied this reaction over hydroxyapatite catalysts, have proposed that this reaction takes place between an alcohol molecule adsorbed on a basic site and a ketone molecule adsorbed on an acid site. In our studies considerable amount of acetone is obtained even over pure alumina, although isopropanol alone does not give acetone under these conditions. Some cyclohexanol is also obtained obviously due to the hydrogen transfer reaction which should be taking place on only the weak acid sites as such hydrogen transfer has been observed even over the highly sodium-impregnated catalysts. The hydrogen transfer reaction over the sodium-impregnated catalysts takes place at the expense of the condensation reaction. This implies that the alcohols adsorbed on acid sites prevent the condensation reaction which require both acid and base sites.

The presence of cyclohexanol in the reaction product of the isopropanol-cyclohexanone mixture suggests that the alcohol-ketone hydrogen transfer reaction requires weaker acid sites than the ketone-ketone hydrogen transfer reaction. This is probably because in the alcohol-ketone hydrogen transfer reaction a hydride ion has to be abstracted from a CHOH group, while in the case of the ketone-ketone hydrogen transfer reaction the hydride ion abstraction has necessarily to be from a $>CH_2$ group which would require stronger acid sites as compared to the CHOH group. The question then arises whether in the ketone-ketone hydrogen transfer reaction the transfer of a hydride ion from a more stable CH_2 to a C=O group to give a less stable CHOH group is possible at all. The reaction may therefore take place without cyclohexanol being an intermediate, cyclohexene being formed immediately after the hydride transfer. The failure to obtain cyclohexanol in the reaction products of cyclohexanone although it is found in the presence of cyclohexanone-isopropanol mixtures also suggests that cyclohexanol is not an intermediate in the reaction of cyclohexanone over alumina catalysts to give cyclohexene.

In this context the results of Crandall and Lin (1968) are instructive. These authors have studied the formation of substituted olefins without the intervention of alcohols during the reaction of tert-butylethylene with tert-butyllithium. They have proposed the following mechanism for the formation of trans-di-tertiarybutyl ethylene by the reaction of tert-butylethylene with tert-butyllithium (reaction (3)).

They have attributed the formation of olefin in the last step to the high heat of formation of lithium oxide. They have also suggested that similar reactions may take

place with organo-metal derivatives of aluminium and other metals which have a high heat of formation of the oxides. In view of the above mechanism it seems likely that a species similar to VIII in reaction (3) may be the precursor to cyclohexene during the reaction of cyclohexanone over alumina.

5. Conclusion

5.1. *Mechanism of the formation of the condensation products*

Our studies with carbon dioxide and with cyclohexanol and isopropanol show clearly that dual strong base-weak acid sites are involved in initiating the condensation reaction. Both the hydrogen transfer reaction between alcohols and ketones and the formation of basic products in the presence of ammonia take place at the expense of the condensation reaction. This implies that both acid and base sites (which may be dual acid-base sites with strong acid or base component) are participating in the condensation reaction. The acid site is involved in the adsorption of the carbonyl group. The reaction of cyclohexanone to give the condensation products may be visualised as follows:
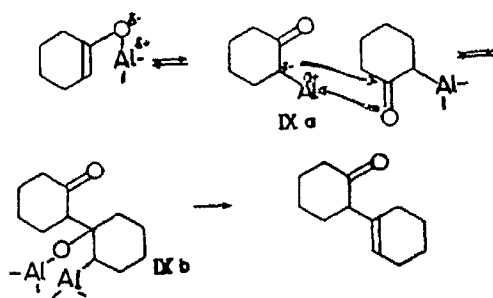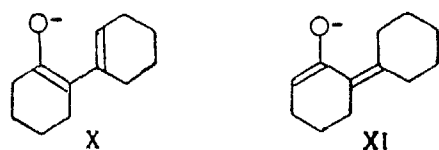

Figure 2a. Reaction sequence for the formation of the dimer.

It is seen from figure 2a that although the enolate structure (VIIc) is more stable than the carbanion structure (VIIb) it has to go through the latter in order to give the condensation products by reacting with another cyclohexanone molecule adsorbed on a weak acid site (IXa) probably via an intermediate surface state (IXb).

In the presence of strong acid sites the protons of both the active methylene groups may take part in the condensation reaction so that a polymer is quickly formed on the surface. Comparing the enolate structures X and XI of the dimeric condensation products 2-(1-cyclohexen-1-yl) cyclohexanone and 2-cyclohexylidene-cyclohexanone respectively, it can be seen that the formation of XI implies the abstraction of a proton from a second methylene group and in such circumstances a polymer would be rapidly formed so that the dimer corresponding to XI is not obtained.

5.2. Mechanism for the formation of cyclohexene from cyclohexanone

As mentioned earlier, since strong acid sites are necessary for the ketone-ketone hydrogen transfer, it is likely that a hydride ion transfer is responsible for the reaction. From the literature it is seen that the formation of olefins from ketones having the same number of carbon atoms is favoured when a β-carbon atom is present (Adkins and Watkins 1951; Blouri and Ahmadi 1969). The site from which hydride ion abstraction takes place is most likely the β-carbon atom. The carbanion formed at the active methylene group on the loss of a proton to a basic site on the surface facilitates the abstraction of a hydride ion from the β-carbon atom. Similarly, the $>C=O$ group when adsorbed on a strong acid site gives a $>C^+—O—$ species which can abstract hydride ion more easily. A simplified mechanism incorporating the ideas given above is shown below (figure 2b):

In the above mechanism, the species XIIa and XIIb are, respectively, combined forms of the species VIc and VId formed on the acid sites with the species VIIb which is formed on basic sites. The failure of carbon dioxide and cyclohexano to influence greatly the reaction of cyclohexanone over strongly acidic aluminas should, as mentioned earlier, be attributed to species of the type XIIa or XIIb. As mentioned earlier, the species XIIa would be more favourable for the hydride ion abstraction because of the presence of the $=C^+—O—$ group. XIIc and XIId resemble the species VIII in the mechanism of Crandall and Lin (1968) (eq. (3)). The high heat of formation of aluminium oxide then gives cyclohexene directly without the intermediacy of cyclohexanol.

In figure 3 the same reaction sequence as in figure 2b is shown in a more idealized manner, this time approximating the sizes of the various species involved (Pauling). The size of the oxygen atom of the carbonyl group is approximated by the size of the
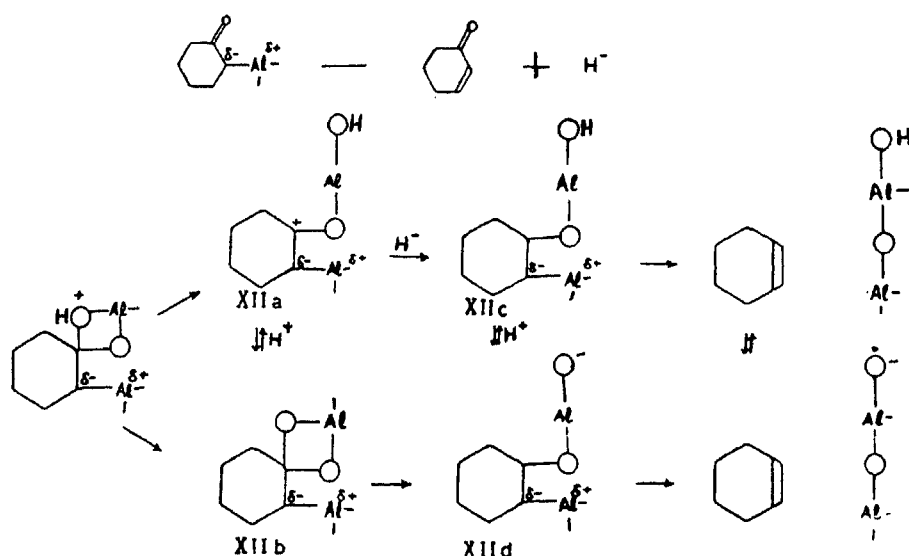

Figure 2b. Reaction sequence for the formation of cyclohexene.

bond as drawn in the figures. A chain of sites are shown, not necessarily linear or even connected. The more acidic aluminium ions are exposed on the surface. The hydride ion, shown as a dotted circle, has a radius greater than 2·0 A (Pauling) and hence it could be transferred in one step across large distances. In figure 3c the hydride ion is shown as displacing the OH⁻ ion. The protons of the —OH groups are quite mobile on the surface and using the mechanism of dehydration of the alumina surface given by Peri (1965) the original alumina surface is recovered. The rate of dehydration of the surface would depend on the temperature and hence the effect of temperature would in effect be an increase in acidity.
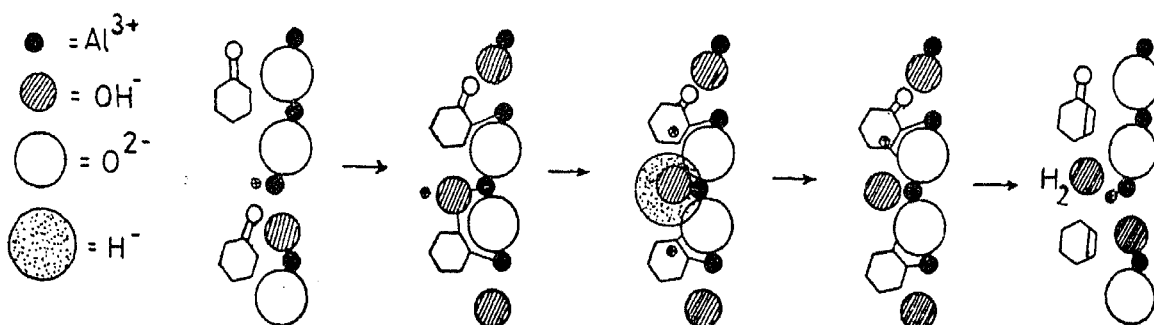

Figure 3. Reaction sequence for the formation of cyclohexene. Radius of the circles corresponds to approximate radius of the corresponding ion.

Acknowledgements

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