Reactions of ketones on oxide surfaces III. Influence of the porous texture of the catalyst

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Abstract

The reaction of cyclohexanone was investigated over several alumina catalysts having markedly different pore-sizes as determined from the adsorption-desorption isotherms at liquid nitrogen temperatures. The activity for the conversion of cyclohexanone did not seem to depend on the pore-size. The catalysts with narrow pores, however, favour the formation of the end products.

Key words: Cyclohexanone, ketone, porous texture, catalyst.

1. Introduction

While investigating the reaction of cyclohexanone over alumina catalysts,[1] the question had arisen whether the dimeric aldol condensation products or the polymeric products formed during the reaction could be condensed in a liquid state in the capillaries of the alumina catalysts. The pore-size distribution of the alumina catalysts could then influence the distribution of the products which are mainly cyclohexene, phenol, and the dimer 2-(1-cyclohexen-1-yl) cyclohexanone. Ivanov et al.[2] had found that the activity of metal phosphate catalysts for the condensation of acetaldehyde depends on the pore-size of the catalyst. The higher condensation products block the pores of the catalysts and screen the surface of the catalyst from the reactant molecules. In this paper we report the preparation and characterisation of four alumina catalysts with very different pore-size distributions, and their effect on the reaction of cyclohexanone.

2. Experimental

Catalysts : Four different alumina catalysts were prepared and labelled as alumina-*A*, -*B*, -*C*, and -*D*.

Alumina-*A* was prepared by the hydrolysis of aluminium isopropoxide. Freshly distilled aluminium isopropoxide (200 g) was added in small quantities to two litres of doubly distilled water with stirring which was continued overnight. The precipi-

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tate was washed several times with doubly distilled water and allowed to stand for three days under doubly distilled water. The precipitate was then filtered and dried at 110° C for 72 hours. The dried hydrate was powdered, sieved to get particle sizes between 40 and 60 mesh, and then activated by heating in air at 500° C for 24 hours.

Alumina-*B* was prepared by the neutralisation of a sodium aluminate solution. However, instead of passing carbon dioxide, acetic acid was added. 50 g of pure aluminium foil was dissolved in two litres of a three molar solution of sodium hydroxide. The suspended impurities were filtered off. The solution was then neutralised with concentrated nitric acid solution till a faint white permanent precipitate appeared. The precipitate was filtered off. To this neutralised solution glacial acetic acid was added in drops till precipitation was complete. The precipitate was washed several times with doubly distilled water and then allowed to stand under doubly distilled water for three days. The precipitate was then filtered, dried, sieved, and activated as described for alumina-*A*.

Alumina-*C* was prepared from a sodium-aluminate solution neutralised by nitric acid as described above. However, instead of adding acetic acid to the solution, the neutralised solution was added all at once into a three litre beaker containing 500 ml of a twenty per cent solution of glacial acetic acid. The precipitate thus obtained were very fine and it took a long time to filter. The precipitate was washed several times with doubly distilled water, dried, sieved, and activated as described for alumina-*A*.

Alumina-*D* was prepared from aluminium isopropoxide. Two litres of a twenty per cent solution of glacial acetic acid was taken and 100 g of freshly distilled aluminium isopropoxide was added. This resulted in a dissolution of the aluminium compound. To this solution twenty per cent ammonia solution was added in drops, till a gel-like precipitate was formed. This gel was washed several times with water dried, sieved, and activated as described for alumina-*A*.

Materials : Cyclohexanone, cyclohexanol, cyclohexene, and cumene of AR grade were distilled ˙o give spectroscopically pure compounds and were used for the investigations.

Nitrogen was obtained from cylinders stated to be more than 99% pure and was further purified by passing over copper turning kept at 700° C.

Apparatus : A conventional BET apparatus was used for the determination of the surface area of the catalyst, and for the adsorption-desorption isotherms of nitrogen at liquid nitrogen temperature. The temperature of the liquid nitrogen was measured using a nitrogen gas thermometer.

The flow system used for the catalytic reactions employed a slanting reactor and was essentially of the design of Upreti *et al.*[4] 2 g of the catalyst in 40 to 60 mesh size were used for the catalytic experiments.

Analysis : The reaction products were collected in a salt-ice freezing mixture and estimated gas-chromatographically using various columns.[1] For the reactions with cyclohexanone, the polymers and "biphenyls" present in the catalysate was estimated by taking the unaccounted weight from the chromatogram. The weight per cent of the polymers and "biphenyls" in the reaction products was taken approximately to be equal to the mole per cent of cyclohexanone reacting to form them. The mole per cent of cyclohexanone reacting to form the rest of the products was then normalised for getting hundred per cent total of the converted cyclohexanone. The accuracy reported in the tables is the accuracy to which the relative distribution of the products such as cyclohexene, phenol, cyclohexenone, and the dimer was estimated. It is for this reason that the values given for the extent of conversion of cyclohexanone is rounded off to whole numbers. There is some coking on the surface and hence the material balance is never better than 98%. Under the same flow rates the material balance was the same (within 1%) for all the alumina catalysts.

3. Results and discussion

Characterization of the catalysts: The pore-size distribution of the alumina catalysts were determined using the method of Lippens and de Boer.[5] The results are shown in Fig. 1 *a*. The *t*-curve method[6] was also employed to get the pore-size distribution and the results are shown in Fig. 1 *b*. It is seen from the figures that alumina-*C* has the narrowest pores followed by alumina-*D*, alumina-*B* and finally alumina-*A*. It is interesting to note that alumina-*D* and alumina-*C* have a very sharp range of pore-sizes which are also quite narrow and stable to sintering compared to the catalysts *A* and *B* which are prepared by conventional methods. Alumina-*D* and -*C* catalysts are stable towards sintering, the surface area quoted for these catalysts in Table I being those for the sintered catalysts.

The alumina catalysts showed lines characteristic of *η*- and *γ*-aluminas. Alumina-*A* and alumina-*B* were predominantly of the *η*-form, while the alumina-*C* and alumina-*D* catalysts were predominantly of the *γ*-form.

The acidity of the catalysts were characterised by alcohol dehydration, cyclohexene isomerisation and cracking of cumene (Table I). The results show that the acidity of the alumina catalysts increase in the sequence alumina-*B* < alumina-*C* < alumina-*D* < alumina-*A*. The lower acidity of the alumina-*B* and alumina-*C* catalysts are probably due to the preparation being carried out in the presence of sodium ions which are known to poison acid sites.[3] It is seen from the above results that there is no particular relation between the pore-size, surface area, or crystal structure to the activity of the catalysts for the several reactions given in Table I. Hence the reactivity of the catalysts for the conversion of cyclohexanone has not been normalised with respect to the surface area of the catalysts.
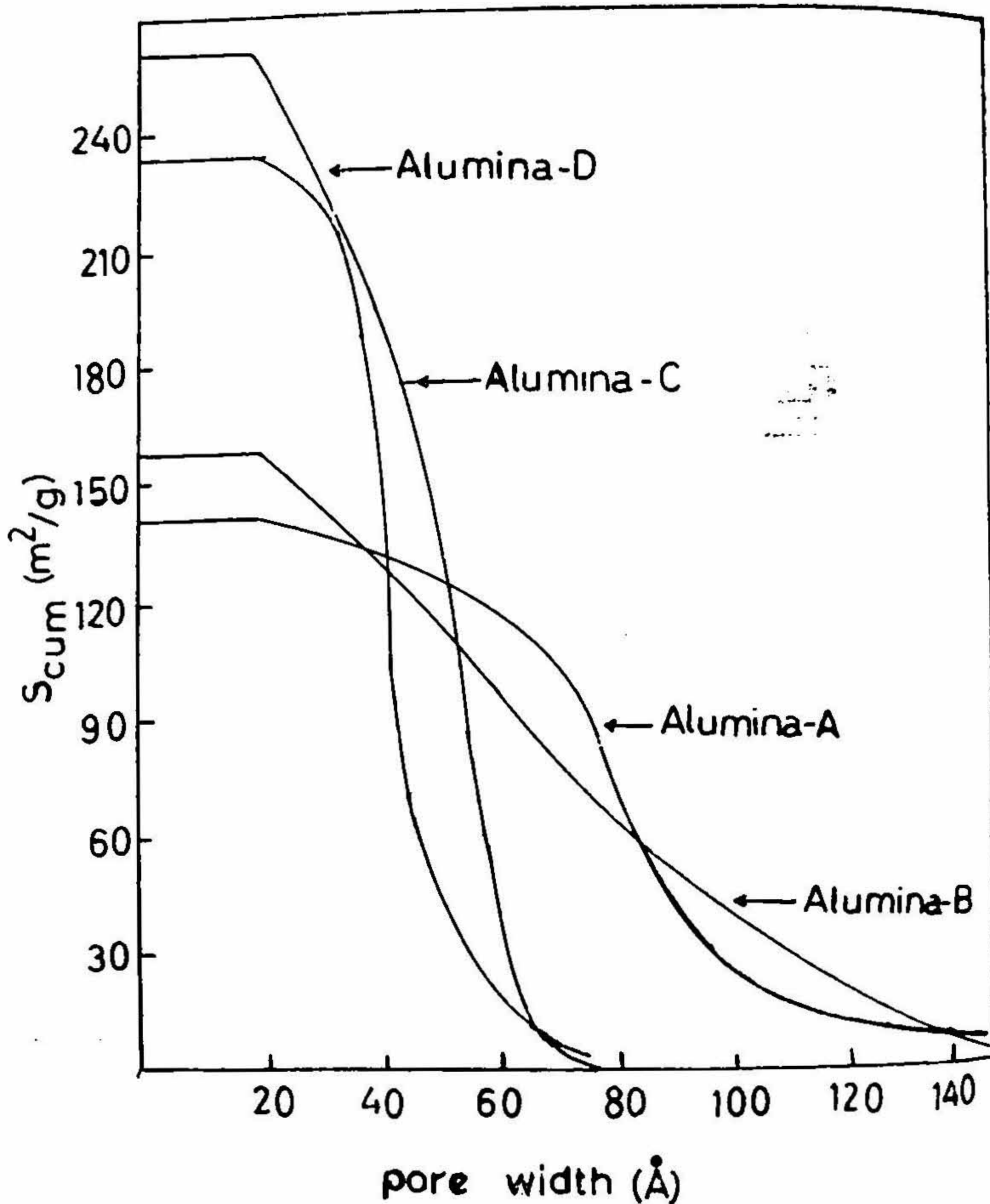
FIG. 1 *a*. S_{cum} plots for the various aluminas.

Reaction of cyclohexanone: The results of the reaction of cyclohexanone over the alumina catalysts are given in Table II. These results are typical of several reactions carried out under various conditions. What is of importance in this study is the distribution of the products primarily as the size of the pores can have an important influence on the distribution[7].
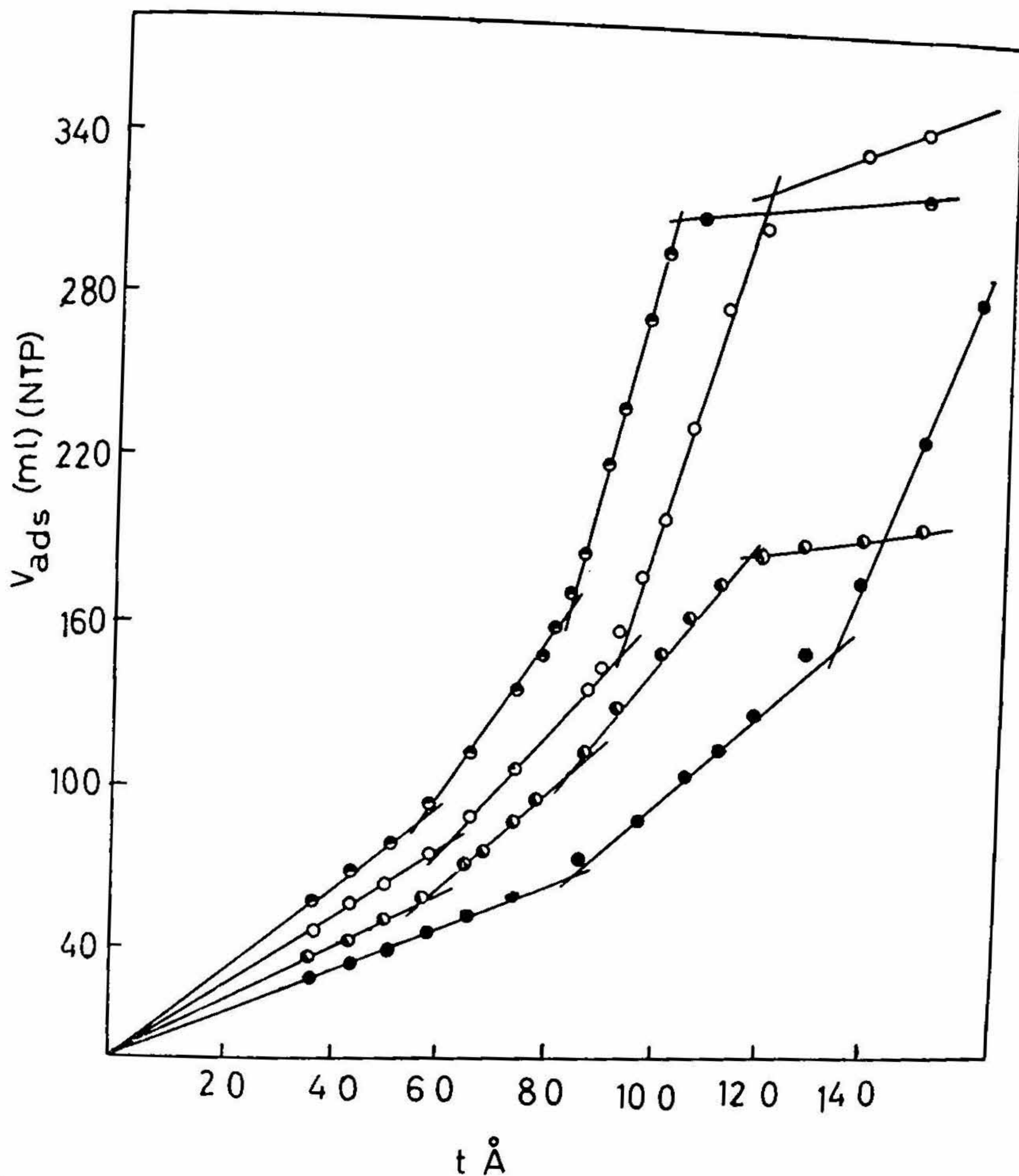
FIG. 1 b. $V_a - t$ plots for various aluminas. $\mathbb{O}$ = alumina-A, $\bullet$ = alumina-B, $\ominus$ = alumina—C, $\bigcirc$ = alumina-D.

It can be seen from Table II that the activity of the catalysts for the conversion of cyclohexanone increases in the increasing order of their acidity, i.e., alumina-B < alumina-C < alumina-D < alumina-A. The per cent conversion of cyclohexanone to cyclohexene increases with decreasing pore-size except for alumina-B. Alumina-C and alumina-D which have the narrowest pores do not give any dimer but there is a significant amount of biphenyls or hydrogenated biphenyls in the product and this

Table I

Characterisation of the Alumina catalysts

Catalyst	Surface area m^2/g	% conversion*		
		cyclohexanol	cyclohexene	cumene
Alumina-A	141	100	35	13
Alumina-B	176	94	2	1
Alumina-C	271	100	6	2
Alumina-D	233	100	24	8

* Cyclohexanol dehydration at 250° C; cyclohexone isomerisation at 350° C; cumene cracking at 480° C.

$WHSV^{-1}$ for all these experiments was 0·093 hr.

Table II

Influence of pore size of the catalyst on the reaction cf cyclohexanone[a]

Catalyst	Cyclo-hexa-none[b]	Products mole % of cyclohexanone reacted					
		cyclo-hexene	phenol	cyclohexe-none	dimer	polymer	
Alumina-A	73	67·8	7·4	6·4	8·1	10·3	3·20
Alumina-B	79	54·1	3·2	10·1	14·2	18·4	3·30
Alumina-C	77	78·7	13·3	2·6	..	5·4*	2·70
Alumina-D	75	77·4	12·4	2·4	..	7·8*	2·83

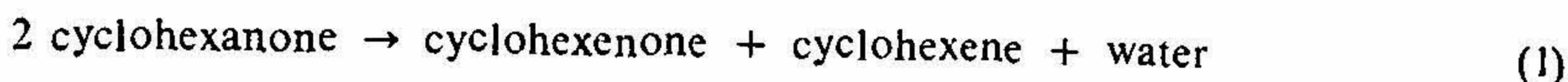a : Feed = cyclohexanone; $WHSV^{-1} = 0·090$ hr.; Temp. = 320 ± 2° C.

b : Weight per cent of cyclohexanone in the catalysate.

c : (mole per cent of cyclohexene)/(mole per cent of cyclohexenone + 2 mole per cent of phenol)=

* ; Significant amounts of biphenyls and hydrogenated biphenyls in the products,
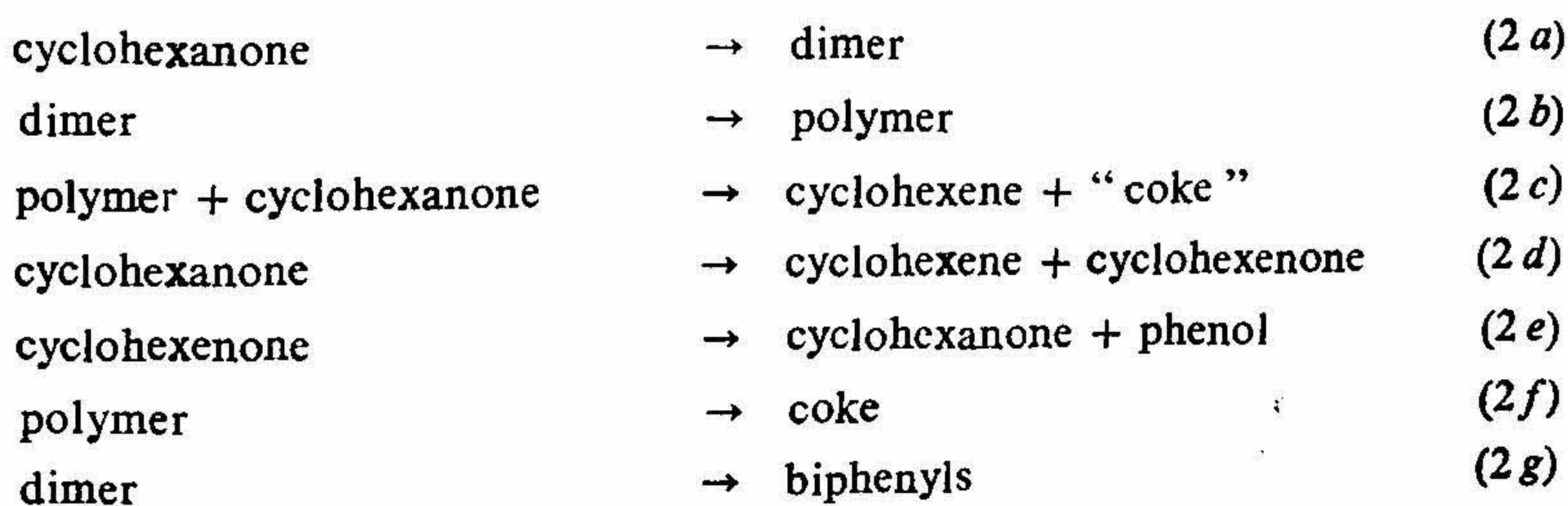
suggests that the dimeric condensation products are converted to the hydro-carbons.

It is also found that alumina-C and alumina-D give a much lower value of the factor ϕ which is a measure of the disproportionation reaction shown below of cyclohexanone to cyclohexene and phenol:

$$2 \text{ cyclohexanone} \rightarrow \text{cyclohexenone} + \text{cyclohexene} + \text{water} \qquad (1)$$

$$2 \text{ cyclohexenone} \rightarrow \text{cyclohexanone} + \text{phenol}.$$

Thus each mole of phenol by the above reactions gives rise to two moles of cyclohexene while each mole of cyclohexenone in the product would give rise to only one mole of cyclohexene. If only the disproportionation reaction was operative then ϕ would be equal to one. A value higher than one shows that some other process is operative and it has been suggested[1] that this is a "cocking" process in which the hydrogen atoms of a polymer formed on the surface are used to reduce cyclohexanone to cyclohexene. The possibility of phenol being retained on the surface is not considered here primarily because, in the context of the results presented in this paper, both alumina-C and alumina-D which have different acidities and hence should retain phenol to different extents, give low values of ϕ.

The reaction sequence of cyclohexanone on alumina has been proposed to be as follows :[1]

cyclohexanone	$\rightarrow$ dimer	(2 a)
dimer	$\rightarrow$ polymer	(2 b)
polymer + cyclohexanone	$\rightarrow$ cyclohexene + "coke"	(2 c)
cyclohexanone	$\rightarrow$ cyclohexene + cyclohexenone	(2 d)
cyclohexenone	$\rightarrow$ cyclohexanone + phenol	(2 e)
polymer	$\rightarrow$ coke	(2 f)
dimer	$\rightarrow$ biphenyls	(2 g)

At low temperatures and contact times (2 c) is the main pathway for the formation of cyclohexene, while (2 d) becomes important at high contact times and temperatures. Under these conditions (2 f) and (2 g) also become important.

The results in Table II can be interpreted in accordance with the above reaction sequence. Wheeler[7] has discussed the selectivity of catalysts for consecutive and simultaneous reactions in terms of their pore width. A consequence of this theory is that for consecutive reactions, the effect of narrowing the pore size is to favour the end product, or in other words to effectively increase the contact time, whereas for irreversible simultaneous reactions there is not much effect. Thus the end products of the reaction such as biphenyls, phenol, would be favoured with the catalysts with narrower pores.

Since the disproportionation reaction (1) is favoured at higher contact times the lower value of ϕ with the alumina-C and -D catalysts is due to the more number of collisions of cyclohexanone in the narrower pores of these catalysts. At the same time reaction 2 f which is the intrapolymeric coke formation by hydrogen transfer within the polymer itself, would exhaust the hydrogen necessary for reaction (2 c) so that reaction (2 d) [or reaction (1)] becomes the only route for the formation of cyclohexene.

Apart from the favouring of the end products of the reaction, the effect of narrowing of pores of alumina does not lead to a screening of the surface from the reactant molecules, by a physical blocking up of the pores by high boiling polymeric products, as proposed by Ivanov et al.[2]

4. Acknowledgements

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