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Carbonized Products of Cumene Catalysed by Nickel Alumina

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The 14.00% Ni–Al_2O_3 catalyst was prepared by the co-precipitation of mixed hydroxides from their nitrate solutions. The surface area S_{BET} and X-ray diffraction analysis were carried out. The analysis of nitrogen adsorption data gave a value of 122.8 m^2g^{-1} for S_{BET}. The values of d-spacing obtained from the X-ray analysis were examined and the catalyst type was determined at 500°C.

The heterogeneous kinetics of cumene conversion was studied on a Ni–Al_2O_3 catalyst using a flow technique under normal pressure. The catalyst activity was measured in the temperature range 400–480°C at space velocities ranging from 7.3 to 12.5×10^{-2} ml min^{-1}. The gaseous products of the conversion reaction were hydrogen, methane and propene, and the liquid products were cyclohexane, cyclohexene, benzene, toluene and cymene together with unreacted cumene. The kinetics of the gaseous products and the cyclohexane, cyclohexene, cymene and toluene revealed a zero order reaction, but that of benzene did not. The polymolecular mechanism was proposed.

INTRODUCTION

The polymolecular mechanism of the heterogeneous catalytic conversion of cycloalkanes and cycloalkenes over nickel-alumina catalyst in flow system under normal pressure was proposed in the previous work[1,2] According to this mechanism the intermediate, polymolecular catalytic complex, $\{An\}^{K_{ads}}$, where n is the number of molecular A chemically connected and adsorbed on the catalyst surface, decomposes in different ways, according to the kinetic conditions, giving the reaction products. It is known[3] that cumene can form condensation products during its catalystic cracking over different catalysts.

In the present work, the heterogeneous catalysis of cumene conversion over Ni–Al_2O_3 catalyst was studied in flow system under normal pressure. The textural characteristics of the catalyst were also studied.

EXPERIMENTAL

The nickel-alumina catalyst was prepared by coprecipitation of mixed hydroxides from their nitrate solutions, using 5M NaOH solution, following the method given by Anderson[4]. The gel obtained was washed thoroughly, dried at 120°C and then crushed, the sieve fraction 0.25–0.5 mm was employed in the surface and catalytic activity measurements.

Chemical analysis of the prepared solid, using the reported method[5], indicate a nickel content of 14.00% by wt, which was consistent with the result given by the spectrophotometric analysis of the catalyst using a Pye Unicam SP 90 series 2 atomic absorption spectrophotometer. The cumene was provided from Recta pure laboratory chemicals, and it was found to be chromatographically pure.

Adsorption Measurements and X-ray Diffraction Analysis

(i) *Adsorption measurements*: The adsorption-desorption isotherm of nitrogen at –195°C was determined using a conventional apparatus[6].

(ii) *X-ray diffraction analysis*: The X-ray diffraction patterns of the catalyst sample and its thermal products after calcination for 4 hrs at 400, 500 and 750°C in dry air were obtained using a Philips model PW 1050 X-ray diffractometer at $\lambda = 1.54 \times 10^{-10}$ m (Powder Diffraction File)[7]. A CuK_α target with a nickel filter was used. All the diffraction patterns were measured at room temperature; the peak was recorded in a single run.

Kinetic study

The catalytic activity was measured using a flow technique. A silica tube (quartz) reactor with an internal diameter of 12 mm is heated by a tubular furnace, the temperature of which is controlled to ± 0.1°C. The reactor and the furnace are mounted in an inclined position[1,2]. Blank experiment without the catalyst was carried out to examine the catalytic effect of the quartz tube in the conversion of cumene. The results of this experiment were compared with the results obtained when the catalyst was used.

The catalyst sample (volume 1 ml) was introduced into the quartz reactor and was activated *in situ* by calcination at 500°C for 4 hrs in a current of dry air free from CO_2 (Ni–AlO). The activated catalyst was then cooled from the activation temperature to the catalytic reaction temperature. The activation temperature for the catalyst samples was chosen as 500°C since thermogravimetric analysis indicated that the solid lost its water of crystallization and hydroxylation at 350°C.

The reactant was introduced using a microdose pump (Unipan 335 A) and the speed of feeding was varied in the range 7.3 to 12.5×10^{-2} ml min^{-1}, and the reaction temperature was in the range 400°–480°C.

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

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

RESULTS AND DISCUSSION

Textural Characteristics of Ni–Al_2O_3 Catalyst

(i) *Surface study*: The surface area S_{BET} was calculated using the conventional Brunauer-Emmett-Teller (BET) equation[8] and it was found to be 122.8 m^2/g. This surface area value was compared with the area obtained by the V_1–t method[9]

The adsorption-desorption isotherm of nitrogen at –195°C on the nickel-alumina catalyst appears to be type IV isotherm of the Brunauer- Deming- Teller classification[10] for mesoporous solids.

(ii) *X-ray study of the solid sample*: The d spacing of the peaks obtained by X-ray diffraction at 500°C were compared with the values given in the ASTM cards[7], and they refered to nickel oxide and α–alumina d-spacing, Fig (1). The average crystalline dimension (t value) was calculated for the catalyst samples calcined at different temperatures at 100% intensity by applying the following expression[11] for the breadth in terms of the crystallite size

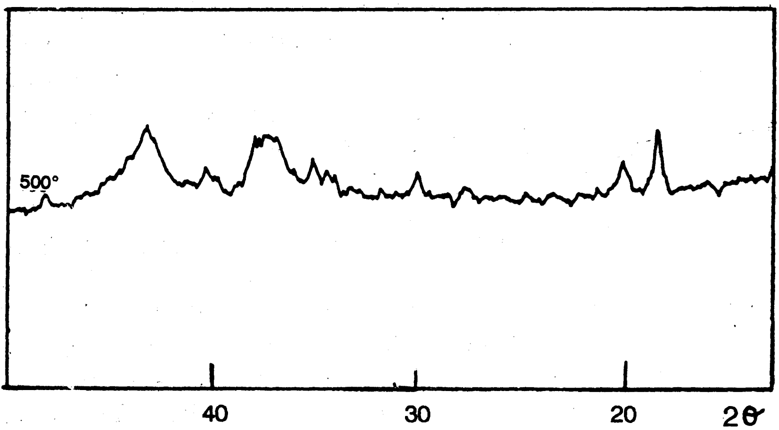


Fig. 1 X-ray diffraction patterns for Ni-AlO catalyst, thermally treated at 500°C

$$\beta = K\lambda / t \cos\theta$$

where β is the peak width at half-intensity, t is a linear dimension of the crystallite and K is a numerical constant of the order of unity, known as Scherrer constant and depends on the crystallite shape, t is commonly defined as the average crystallite dimension measured in a direction normal to the reflecting planes, and its calculated value was found to be 3.11×10^{-10} m.

The Heterogeneous Kinetic Studies

1. Effect of space velocity:

The reaction temperature was monitored at 400°C, and cumene vapour was allowed to pass over 1 ml of the Ni–Al catalyst at space velocities ranging from 7.3 to 12.5×10^{-2} ml/min. This experiment was repeated at 430, 450 and 480°C over fresh portions of Ni–Al_2O_3 catalysts pretreated with dry air (Ni–AlO)

The volume of the gaseous products (V, ml/min) was determined at various intervals. When this volume was plotted against time a straight line was obtained, the slope of which gave the rate of formation of the gaseous products, which was then corrected to standard temperature and pressure (V^o, in millilitres per minute). Fig.-2 shows the effect of variation in the time of contact τ ($\tau = 1/f$, where f is the space velocity) on V^o (the rate of formation of gaseous products at STP).

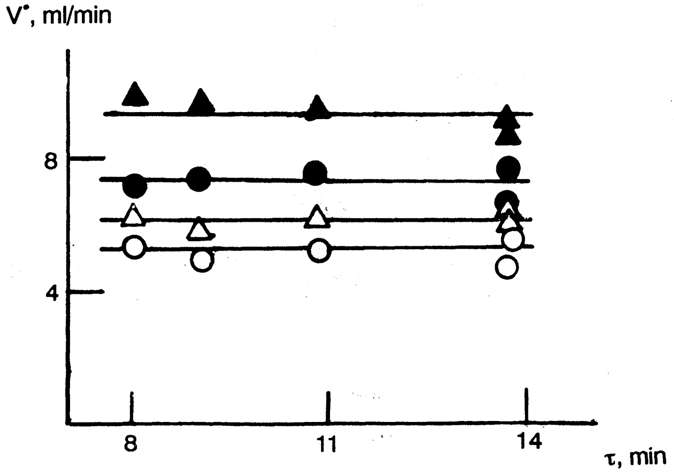


Fig. 2 The effect of variation of time of contact on the rate of formation of gaseous products, V°, at (O) 400°C, (Δ) 430°C, (●) 460°C and (▲) 480°C.

The gaseous products were found to be hydrogen, methane and propene, and the liquid products were found to be cyclohexane, cyclohexene, benzene, toluene and cymene together with unreacted cumene. The % formation of each of the liquid products was calculated from the chromatographic analysis. From Fig.-3 and the data given in Table-1, the following can be predicted:

The rates of formation of gaseous products, cyclohexane, cyclohexene, toluene and cymene are independent of the contact time, *i.e.* zero order, for Ni-AlO catalyst, at temperatures from 400–480°C. The rate of formation of benzene and the % of unreacted cumene depend on the space velocity, *i.e.*, the % of formation of benzene increased with the increase in time of contact for Ni-AlO. This indicates the disorder of the stoichiometry of conversion of cumene and the complexity of the catalysis mechanism.

The presence of the different liquid products of the catalysis of cumene obtained under our experimental conditions and indicated by the analyses suggested that three processes may have taken place.

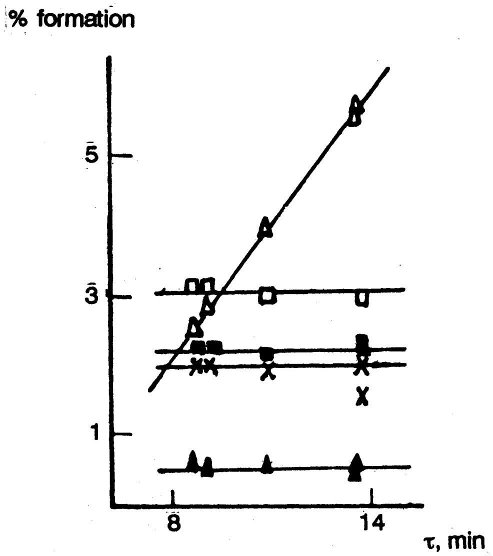


Fig. 3(a) The effect of variation of time of contact on the formation of liquid products in the catalystic conversion of cumene on Ni-Al_2O_3 catalyst at 430°C. (■) cyclohexene, (Δ) benzene, (▲) toluene, (□) cymene, (X) cyclohexane.

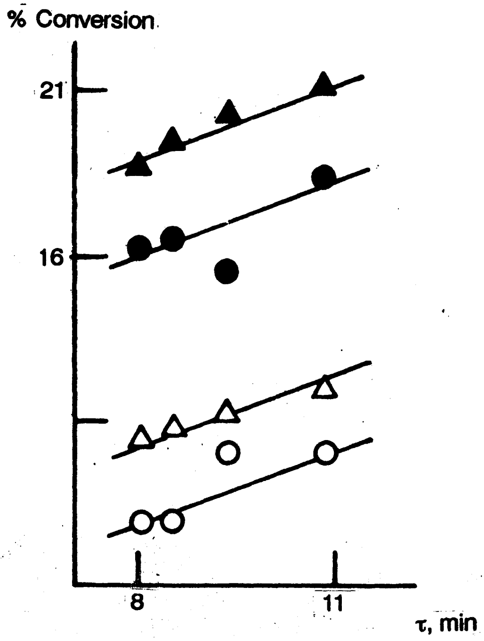
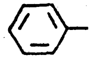
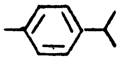
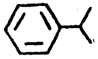


Fig. 3(b) The effect of variation of time of contact on the conversion of cumene on Ni-Al_2O_3 catalyst at (O) 400°C, (Δ) 430°C, (●) 460°C and (▲) 480°C.

TABLE 1
THE EFFECT OF SPACE VELOCITY ON THE CATALYTIC CONVERSION OF CUMENE ON Ni–AlO CATALYST PRETREATED BY DRY AIR AT 500°C IN FLOW SYSTEM UNDER NORMAL PRESSURE.

Temp. °C	f × 10^2 min^{-1}	V° ml/min	Conv. %	ΔE kJ mol^{-1}	Wt. %	Analysis of liquid products, %					
											
400	7.30	5.60	9.96	38.5	15.79	Traces	1.43	5.76	0.37	2.40	90.04
	9.30	5.20	10.00			0.95	1.29	4.24	0.44	3.08	90.00
	11.10	5.00	8.09			0.85	1.56	2.50	Traces	3.18	91.91
	12.50	5.40	7.81			0.81	1.59	2.10	Traces	3.31	92.19
	7.30	4.70	9.92			Traces	1.64	4.92	0.39	2.97	90.08
430	7.30	6.00	12.00	38.5	16.17	1.51	2.19	5.00	0.50	2.80	88.00
	9.30	6.20	11.13			1.86	2.05	3.98	0.47	2.77	88.87
	11.10	5.80	10.79			2.16	2.12	2.78	0.49	3.15	89.21
	12.50	6.20	10.41			2.07	2.20	2.50	0.62	3.02	89.59
	7.30	6.50	10.17			2.12	2.29	5.20	0.56	Traces	89.83
460	7.30	6.90	18.45	38.5	13.63	2.56	Traces	7.32	2.06	6.51	81.55
	9.30	6.70	15.74			Traces	3.68	3.42	2.18	6.46	84.26
	11.10	7.40	16.39			2.35	3.82	1.67	2.03	6.52	83.61
	12.50	7.20	16.28			2.47	3.88	1.44	2.14	6.35	83.72
	7.30	6.50	17.30			Traces	3.80	7.50	Traces	6.00	82.70
480	7.30	8.60	21.19	38.5	14.28	2.62	4.06	4.45	1.92	7.14	78.81
	9.30	9.50	20.43			2.85	4.23	4.58	1.88	6.89	79.57
	11.10	9.70	19.50			2.76	4.59	3.40	1.97	6.78	80.50
	12.50	9.90	18.72			2.57	4.18	3.03	2.29	6.65	81.28
	7.30	9.20	20.33			2.45	4.45	6.62	Traces	6.81	79.67

(i) cracking (formation of benzene and toluene),
(ii) cracking and hydrogenation (formation of cyclohexene and cyclohexane),
(iii) alkylation (formation of cymene).

The amount of each product was found to depend on temperature and on the kinetic conditions.

The internal relation between the three mentioned processes over Ni-AlO catalyst at 400 and 480°C, the minimum and the maximum of the range of the experimental temperatures, is given in Table-2.

TABLE-2
INTERNAL RELATION BETWEEN PROCESSES (i), (ii) AND (iii).

Temp.	Catalyst	Process (i)	Process (ii)	Process (iii)
400°C	Ni–AlO	61.6%	14.4%	24.0%
480°C	Ni–AlO	31.6%	33.0%	35.4%

It follows from the results that with the increase in temperature the cracking process decreased in 30.0%, the cracking and hydrogenation process increased in 18.7% and the alkylation process increased in 11.3% for Ni-AlO catalyst with the increase in temperature from 400° to 480°C.

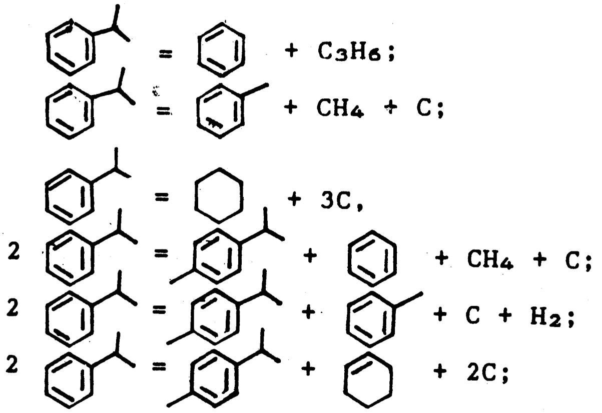
The weight of the catalyst was determined before and after experiment. The increase in weight was calculated taking into consideration the loss in weight due to calcination and is given in Table-1. The apparent weight increase was also found to differ according to the experimental temperature. It can be concluded therefore that the increase in weight depends on the nature of the catalyst and on the kinetic conditions. The significant increase in the mass of the catalyst besides the formation of cymene (Table 1) cannot be explained easily in terms of ion or free radical mechanism. This increase can be accounted for by the formation of polycondensation products, which would be responsible for the apparent increase in weight of the catalyst due to the formation of carbonized products.

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

The data on log V° at the different space velocities determined at various temperatures between 400° and 480°C, allowed us to calculate the apparent activation energy of conversion of cumene (Fig.-4). This energy was determined by plotting log V° versus 1/T (T is the temperature in absolute scale).

Table-1 includes the calculated activation energy ΔE for cumene in contact with catalyst Ni–AlO at each space velocity and at different temperatures. It is evident that the apparent activation energy is almost independent of the time of contact and the working time of the catalyst. An average value of 38.5 kJ/mole for Ni–AlO catalyst was calculated.

It follows from the analysis of the products of catalysis of cumene that besides the mentioned three processes the following reactions are possible:

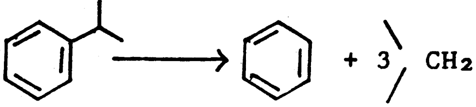


(1)
(2)
(3)
(4)
(5)
(6)

Processes (1) to (3) represent monomolecular reactions, *i.e.* complete cracking, to form the different products.

Processes (4) to (6) are bimolecular reactions at which cymene is produced.

All these processes are possible from thermodynamic point of view. Cumene may also decompose acccording to:



(7)

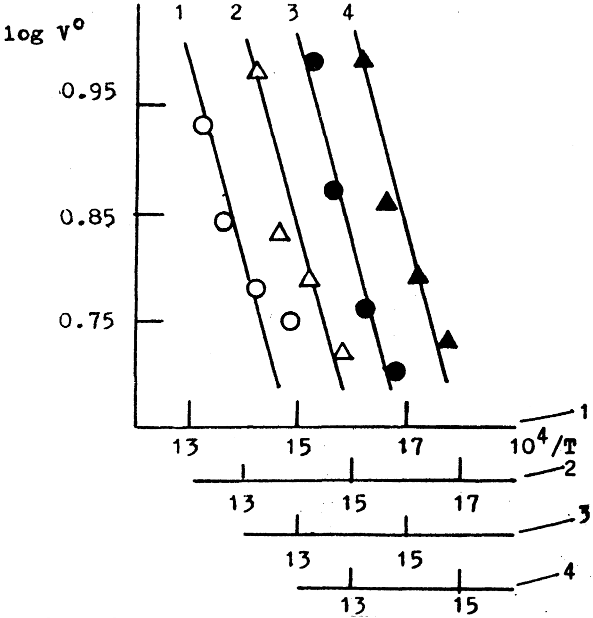


Fig. 4 The effect of temperature on the catalytic conversion of cumene on Ni–Al$_2$O$_3$ catalystic pretreated by air at 500°C, (1) $f = 7.30 \times 10^{-2}$ min^{-1}, (2) $f = 9.30 \times 10^{-2}$ min^{-1}, (3) $f = 11.10 \times 10^{-2}$ min^{-1}, (4) $f = 12.60 \times 10^{-2}$ min^{-1}

which indicates the formation of methyl radical. According to Zelinskii *et. al*[12], in the presence of hydrogen the methyl radical is hydrogenated to methane, however, the formation of methyl radicals needs vigorous conditions, which are not satisfied in our experimental conditions.

Therefore, it is difficult to judge the type of intermediate catalytic complex considering the completely covered surface by reactive substance under the normal pressure.

However, the study of heterogeneous catalytic process in flow system under different pressure[13–15] allowed the determination of all kinetic constants and recieving information to check up and deduce new equations, it also made it possible to distinguish between the mechanism of monomolecular and polymolecular catalytic process.

The gain in weight of the nickel-alumina catalyst during the conversion of cumene (Table 1) is suggested to be due to the condensation of cumene molecules on the catalyst and brown resin is observed on the inside walls of the catalytic tube, and also due to the formation of carbon.

It is suggested that all the possible ways of conversion of cumene over nickel-alumina catalyst does not proceed through the formation of intermediate monomolecular catalytic complex, but it proceeds via polymolecular mechanism, through the formation of a polymolecular catalytic complex intermediate according to scheme (1):

$$n\,C_9H_{12} + K \rightleftharpoons \{(C_9H_{12})_n\}^{K_{ads}} \qquad (8)$$

This intermediate decomposes immediately in several ways giving the different products.

$$[(C_9H_{12})_n]^{K_{ads}} \left\{ \begin{array}{l} [(C_9H_{12})_n - kC_6H_6 - kC_3H_6]^{K_{ads}} + kC_6H_6 + kC_3H_6\ (I) \\ [(C_9H_{12})_n - kC_6H_6 - kCH_4 - kH_2 - 1C]^{K_{ads}} + KC_6H_6 \\ \quad + kCH_4 + kH_2 + 1C(II) \\ [(C_9H_{12})_n - kC_{10}H_{14} - kC_6H_{10} - 1C]^{K_{ads}} + kC_{10}H_{14} \\ \quad + kC_6H_{10} - 1C(II) \\ [(C_9H_{12})_n - kC_{10}H_{14} - 1C_6H_{12} - mC_6H_{10} - fC_6H_6 \\ \quad - qC_7H_8 - gCH_4 - rH_2 - pC]^{K_{ads}} + kC_{10}H_{14} + 1C_6H_{12} \\ \quad + mC_6H_{10} + fC_6H_6 + qC_7H_8 + gCH_4 + rH_2 + pC(IV) \\ \text{etc.} \end{array} \right.$$

Scheme (1)

where K indicates the catalyst surface. The decomposition and the desorption is assumed to be one kinetic step which is the rate determining step.

All the results confirm the contribution of condensation products of cumene as intermediate substance in its conversion over nickel-alumina catalyst and ensure the polymolecular mechanism for this conversion. according to the temperature and kinetic conditions, the polymoleclar catalytic complex decomposes in this or that way giving the different products.

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