STUDY OF DEHYDROGENATION OF CYCLOHEXANOL USING DIFFERENT PORE SIZES OF COPPER- THORIUM CATALYST BY IMPREGNATION METHOD

Ratna Sarkar
Department of Chemistry, Sindhu Mahavidylaya, Nagpur, India
ratnasarkar1712@gmail.com

Abstract

Catalytic vapour phase dehydrogenation of cyclohexanol is the key reaction in the industrial production of cyclohexanone. Literature survey reveals that copper is an active metal for dehydrogenation of cyclohexanols, but its activity is accelerated when supported by promoters like oxides of rare earth metals and heavy metals.Fluidised beds was avoided for irregularities in the flow patterns . Therefore the study of vapour phase catalytic dehydrogenation in a fixed bed was proposed. Seven different copper catalysts were prepared by impregnation method on pumice stone. Kinetic runs were carried out using a fix bed reactor with variation in pore sizes to achieve maximum conversion .It was observed that copper cerium oxide with -40 +60 U.S mesh size was selected. Activity and selectivity was studied by carrying out reaction at low temperature to achieve maximum conversion with minimum side reaction.

1. Introduction

Cyclohexanone is an important intermediate in industries , mainly used as solvent for resins, lacquers and dyes. It first prepared by the dry distillation of calcium pimellate and later by Bonveault by catalytic process of dehydrogenation .Most of the studies are carried out with catalysts based on copper formulations under mild conditions of temperature due to copper sintering. certain rare earth oxides were also added. The catalysts were prepared by impregnation method . The stiochometric equations for the dehydrogenation of cyclohexanol are $C_6H_{12}O \rightarrow C_6H_{10}O + H_2O$, where side reactions were avoided but also gave hydrogen as the by product. Further dehydrogenation of cyclohexanone to phenol is also reported but by proper choice of the catalyst , and maintaining optimum operating conditions ,the formation of phenol was practically eliminated.

Fluidized beds were avoided for irregularities in the flow pattern and low space velocities. Hence the study of vapour -phase dehydrogenation of cyclohexanol to cyclohexanone was proposed in a fixed bed of catalysts. Experiments were conducted with copper catalysts using different pore sizes There activity and selectivity were studied .The addition of cerium- oxide to copper promoted its dispersion and stability of the catalysts[1]Finally copper cerium oxide -40 + 60 U.S mesh ,impregnated on pumice stone was selected to obtain maximum conversions.

2. EXPERIMENTAL SECTION

CATALYST, APPARATUS, METHODS

Catalyst was prepared by impregnation method on pumice stone. Copper -cerium oxide was prepared by adding 288 gm of copper nitrate in 100 ml of distilled water and to this 0.9 gm of cerium nitrate was added To this clear solution 100gm of pumice stone of desired -40 + 60 mesh size was added and stirred from time to time and then it was kept for 24 hrs, so that solution enters the pores of pumice stone . The excess solution was decanted and the solution impregnated on pumice stone was dried in an air oven at 110 °C.After drying the impregnated pumice stone was heated at 400 °C for 6hrs and cooled .The catalyst was reduced by passing through hydrogen gas at 275 °C ,till constant weight is obtained . Copper oxide is reduced

to copper and cerium oxide remains unaffected .The catalyst thus obtained has pumice stone as the carrier and the impregnated material was Copper and ceria .In a similar manner Copper -ceria was deposited on pumice stone having -20 +40 U.S mesh and --4 +8U.S mesh sizes . their compositions were quantitatively estimated by titrating against standard sodium thiosulphite solution using starch as the indicator , iodometrically .

$$CuSO_4 + KI \rightarrow CuI + I_2 + K_2SO_4$$
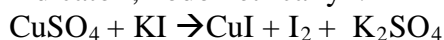
1. APPARATUS

An integral type of glass reactor was chosen to study the effective method of heat distribution . Whithen the glass reactor , isothermal conditions were maintained. The apparatus consisted of Reservoir , Preheated , Reactor , Condensor and product collection unit .

The Reservoir which is the feed system consisted of a 3 litre aspirator bottle ,connected to a flow meter ,placed about 12 feet high above the reactor. The flow of cyclohexanol was controlled through the flow meter . The flow meter was in turn connected to a preheater , insulated by procellain beads and wound with Nichrome heating wire having temperature lower than the reaction temperature . The downstream end of the preheated was connected to the upper part of the main reactor. The vapours of cyclohexanol from the reservoir , passes through the preheater into the reactor containing the prepared copper -ceria oxide catalysts with different flow rates and at a fixed temperature .

2. REACTOR

The reactor was made up of a vertical glass tube of 41mm external diameter ,35mm internal diameter ,2mm thick ,625mm length . it has two thermometer pockets in the middle portion of the reactor. The lower end of the reactor was connected to the double surface water condensers .

The reactor was electrically heated through Nichrome { 24 gauge} wire , wound round it .and also insulated with porcelain beads . To prevent heat loss , the reactor was covered with an asbestos rope lagging .Further the supply of electrical energy was controlled through the regulator The lower part of the reactor was filled with 4mm sizable glass

beads . The copper catalysts of a particular mesh size was then introduced .,which was then again covered up with glass beads of similar sizes , which favored uniform flow distribution. The discharge end of the reactor was connected to the product collection unit through condensers .For condensation of the product cyclohexanone , ice cold water was circulated through the condensers .The product was then analyzed for ketones .A three - way stop cork served to divert the flow of exit gases into the conical flasks .The experimental runs were repeated with copper –ceria catalysts of different pore sizes as shown in Fig 1.
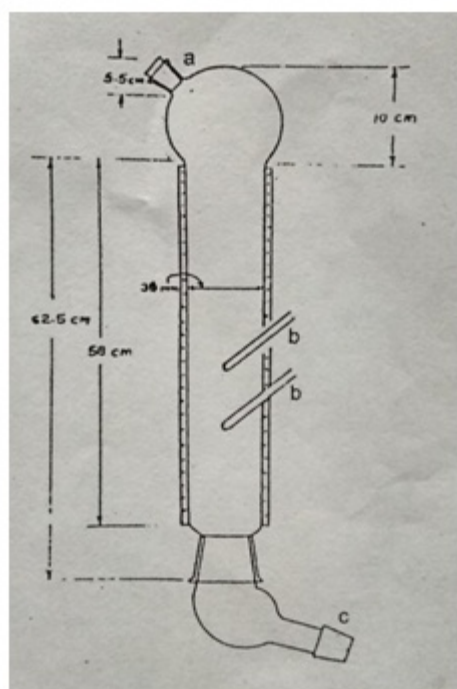

Fig1. Experimental Reactor
Here,
a= connected to the preheater
b=thermometer pockets
c=connected to the condenser

3.ANALYTICAL PROCEDURE

The product cyclohexanone was collected and was estimated by transferring known amount of the sample into one of the conical flask containing hydroxylamine hydrochloride solution with 10 ml bromophenol blue as the indicator and titrated against 1N NaOH until the matched with the blank titration of blue - green colour .

Cyclohexanone = 9.814 x V x N) / V
V = Volume of NaOH
N = Normality of NaOH solution

W = Weight of sample in gm

SAMPLE COLLECTION

Weight of sample = 0.9808 gm

Volume of 1 N NaOH consumes = 3.8 ml

Cyclohexanone % = 9.814 x1 x3.8) / 0.9808= 38 .023 %

Weight of condensed Cyclohexanone = 7.2 gm

Molecular weight of Cyclohexanone =98. 16 gm

Gram moles of Cyclohexanone = 0.38023 x7.2) / 98.16= 0.027889

Gram moles of Cyclohexanone fed = 7.31 /100.16 = .0729

Conversion % =0.027889 / 0.0729) x100 = 38 .25 %

4.TABLE & GRAPH :

| Temp	Feed Rate gm/hr	W/F	Conversion		gm/mole of feed		Hydrogen	Overall Conversion
			Ace	Ket	Ace	Ket		
225	26 .93	108.6	81.01	18. 90	0.8074	0.1926	0.1926	0.1926
	34. 46	85.41	85.36	14.64	0.8510	0.1490	0.1490	0.1490
	59.12	51.2	90.12	9.88	0.8994	0.1006	0.1006	0.1006
	81.50	36.0	95.76	4.24	0.9568	0.0432	0.0432	0.0432
-20+40 U.S.Mesh; w=30gm								
225	29.40	100	74.98	24.02	0.7461	0.2539	0.2539	0.2539
	42.30	69.00	80.80	19.20	0.8054	0.1946	0.1946	0.1946
	63.70	46 .21	87.45	12.55	0.8647	0.1353	0.1353	0.1353
	138.2	21.30	97.30	2.70	0.9734	0.0266	0.0266	0.0266
-40+60 U.S Mesh; w=30gm								
225	23.57	124.8	67.70	32.20	0.6730	0.3270	0.3270	0.3270
	42.54	69.70	79.90	20.10	0.7960	0.2040	0.2040	0.2040
	70.75	41.60	85.04	14.96	0.8482	0.1518	0.1518	0.1518
	144.90	20.31	95.45	4.53	0.9538	0.0462	0.0462	0.0462
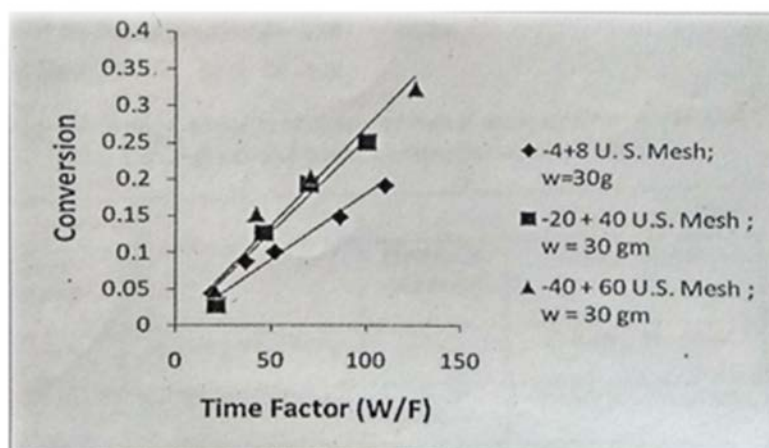
Fig 2. Conversion as a Function of time

5. RESULT & DISCUSSION

1) The effect of time factor on conversion of cyclohexanol to cyclohexanone were investigated. It was observed that where W is the weight of the catalyst and F is the feed rate are variables. When any one of the above variables were changed ,the conversion was

affected .When graph of conversion versus Time factor (W / F) was plotted , it showed that, as time factor increases , the conversion also increased.

2) The conversion were also studied at different temperatures .It was observed that

Low temperature favoured higher conversions

3) In the present investigation , three different mesh sizes were of copper - ceria oxide catalyst were prepared on pumice stone (-4 + 8 ; -20 + 40 ; and -40 + 60 mesh size) and runs were carried out at various values of time factor (W / F). This showed that for smaller particle size of --40 + 60 U.S Mesh , the conversion appeared to be higher than the larger particles of -4 + 8 U.S mesh .

6. REFERENCES

[1] Belskaya , R .I., Komarov ,V.S ., Taborisskaya ,E.A .,Inst. Obshch Neorg., Khim ,Minsk, USSR ,Vesti Akad, Navuk ,BSSR ,Ser. Khim Navuk ,1, 21-25 (1975)

,

[2] Rottig , Walter ,Frohning , Carl. D., Leibern ,Ch. T.Hans .Ger .Offen . Pat .2, 347,17 Apr, (1975)

[3] Kerpenchik , E. V., Belskaya ,R .I ., Potapovich ,A.K ., Berezovik ,G.K ., Inst .Obshch .Neorg. Khim. Minsk . USSR. Vestsi Akad .Navuk ,BSSR .Ser. Khim Navuk , 2, 44 -6 (1983)

[4] Sideltseva ,M .A ., Erofeev ,B , V ., Inst .Fiz. Org . Khim . Minsk .USSR. Westsi .Akad . Navuk , BSSR , Ser . Khim. Navuk . 3, 7—11 (1986)

[5] ,,Minyukova ,T .P ., Simentsova ,I .I ., Khasin , A .V ., Shtertser ,N .V ., Applied Catalysis A ; General 237 , 171---180 (2002)

[6] uArturo Romero ,Pedro Yustos and Aurora Sentos ,Ind .Eng . Chem .Res 42 (16) 3654 -3661 (2003)

[7] Ernesto Simon ,Juana Maria Rosas ,Aurora Santos , Arturo Romero ., Catalysis Today 187 ,150-158 ,(2012)

[8] Santacesaria ,E ., Carotenuto ,G ., Tesser ,R .,Di Serio ,M ., Chemical Eng Journal 179 , 209 -220 , (2012)

[9] Carotenuto ,G ., Tresser ,R., Di Serio ,M ., Santacesaria , E., Catalysis Today ,202 -210 ,(2013)