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ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JULY 2003

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Dehydrogenation of Cyclohexanol to Cyclohexanone: Influence of Methylcyclopentanols on the Impurities Obtained in ϵ-Caprolactam

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The most representative impurities in ϵ-caprolactam produced from cyclohexanol obtained by partial hydrogenation of benzene are the δ-valerolactams. These impurities come from the dehydrogenation−oximation−Beckmann rearrangement of the methylcyclopentanols that are typical impurities in the cyclohexanol obtained from benzene. The dehydrogenation of cyclohexanol is carried out in a fixed-bed reactor with a commercial catalyst based on copper oxide. The evolution of these 1-, 2-, and 3-methylcyclopentanol impurities during dehydrogenation is analyzed separately and in a combined way, and the products are identified and quantified. The cyclohexanone obtained after cyclohexanol dehydrogenation and reaction mixture rectification is taken as a reactant for the oximation and Beckmann rearrangement stages. The evolution of the 1-methylcyclopentanol and 2- and 3-methylcyclopentanones impurities contained on this purified cyclohexanone to the final impurities found in ϵ-caprolactam are analyzed.

Introduction

Cyclohexanone is the intermediate compound employed more in obtaining ϵ-caprolactam. Its use identifies the denominated classic or conventional processes.[1] Cyclohexanone has been mainly obtained by cyclohexane oxidation in the liquid phase and by phenol hydrogenation in the liquid[1] and in the gas phase. In some processes of this type cyclohexanol is obtained in similar quantities as cyclohexanone. Cyclohexanol dehydrogenation in the gas phase with solid catalysts is the procedure used to transform it in cyclohexanone. Therefore, the results obtained in the dehydrogenation have a great technician-economic importance in the ϵ-caprolactam production.

The main destination of the ϵ-caprolactam is to obtain synthetic fibers. The impurities of the monomer have a great influence on the polymerization process to obtain the polyamide. Several authors have reached the conclusion that impurities such as cyclohexanone oxime, cyclohexanone, and aniline modifies the polymer viscosity and density.[2] For this reason great effort has been devoted to develop procedures able to obtain ϵ-caprolactam in great purity.[3,4]

The impurities of ϵ-caprolactam[5] can come from the impurities of the raw material (benzene, toluene, phenol, cyclohexane, etc.), from the products formed in the transformation stages of the reagents (oxidation, hydrogenation, dehydrogenation, oximation, Beckmann rearrangement, etc.), and from the products formed in the separation (distillation stages, extraction, neutralization, etc.). It is desirable that the methods of elimination of the impurities that contain the different intermediate products to obtain the ϵ-caprolactam from the raw material are simple and low incost. The number of impurities, the quantity of impurities, and the nature of the impurities formed are the key factors that should be controlled in all and each one of the stages of the process of ϵ-caprolactam production to make easier their separation and to achieve the high purity of the monomer that is required for the polymerization process.[6]

In the literature, the presence of methyl-δ-valerolactams in ϵ-caprolactam has been described as coming from the oxidation of cyclohexane.[7] In the literature no experimental evidence is given on the origin of these impurities, both from the composition of the cyclohexanol and from the alcohol dehydrogenation process to give cyclohexanone. Therefore, an explanation for the methyl-δ-valerolactams' presence in ϵ-caprolactams should be found. When the dehydrogenation of cyclohexanol to obtain cyclohexanone is carried out, the impurities formed appear from the transformation of the reagent impurities and these will be added to those impurities coming from the process. If cyclohexanone contains methylcyclopentanones, it is unavoidable that they will evolve to the corresponding lactams in the oximation and Beckmann rearrangement stages.

Asahi Chemical Industry Co. has developed a procedure to obtain cyclohexene by partial hydrogenation of benzene with catalysts of ruthenium.[8] The hydration of cyclohexene with zeolites as catalysts leads to cyclohexanol. In this way, there is a new procedure to obtain cyclohexanone,[9,10] from which ϵ-caprolactam is manufactured by the conventional route. Cyclohexene is a compound that yields cyclohexanone with some advantages as compared to the processes that use cyclohexane oxidation or phenol hydrogenation. A very high yield of cyclohexanol could be achieved, a low number of impurities formed in the two transformations, hydrogenation of benzene and cyclohexanol dehydrogenation, and the nature of the impurities allowed them to separate easily and they did not cause a great descent in the quality of the ϵ-caprolactam.

The catalysts used to carry out the cyclohexanol dehydrogenation are mixtures of copper oxides with other compounds such as zinc, chromium, magnesium, manganese, cobalt, or iron oxides on different supports.[11,12] There are studies about the behavior of these types of catalysts in front of the possible reactions: dehydrogenation, hydrogenation, and dehydration. These studies explain the presence of condensation products

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10.1021/ie0210154 CCC: $25.00
Published on Web 07/11/2003

Table 1. Properties of the Dehydrogenation Catalysts

		physical properties			
catalyst	composition (% w/w)	ρ (g cm^{-3})	S_g (m^2 g^{-1})	V_p (cm^3 g^{-1})	size (mm)
C1	CuO. 67−77%.				
Engelhard Cu-0203T	Cu chromite. 20−30% graphite sint. 1−3%	2.0	10	0.10	$d_p = 3.2$
C2					
Engelhard Cu-1230	CuO 15%; $(2CuO)Cr_2O_3$ 44% CrO_4Ba 12%; Al_2O_3 29%	1.05	120	0.36	$d_p = 1.6$ mm

in the reaction mixture. Mendes and Schamal[13] summarizes the different routes of cyclohexanol reaction to explain the formation of benzene, cyclohexene, cyclohexane, and phenol jointly to the cyclohexanone, in metallic and acid centers. High quantities of cyclohexene are formed in the monometallic catalytics, which is due to the influence of the acid centers, while those that contain a second metal favor the dehydrogenation when acting as diluters of the active metal or increasing the selectivity when promoting the bond effect.

Due to the endothermic nature of the dehydrogenation reaction, it is necessary to operate at high temperatures to displace the balance toward high conversions. However, when increasing the operation temperature, a decrease of the selectivity of the process takes place and even a loss of the catalyst stability. It is necessary that the catalyst is able to maintain its stability and selectivity operation at temperatures where the balance conversion is of the order of 50%.

Among the various impurities that can be found in the cyclohexanol coming from the cyclohexene hydratation are the methylcyclopentanols.[13] These compounds are formed by isomerization of cyclohexanol when zeolites are used as catalysts in the cyclohexene hydratation.[14] It is necessary to know the evolution of the methylcyclopentanols to methylcyclopentanones, which remain with cyclohexanone in the dehydrogenation mixture. The transformation of these methylcyclopentanones in methyl-δ-valerolactams during the remaining stages carried out for the ϵ-caprolactam formation must also be considered. The transformation of these impurities affects, besides the transformations and generation of other impurities, the complexity of the purification process and the quality of ϵ-caprolactam.[15]

Experimental Section

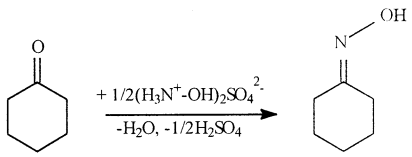
Catalysts. Two commercial catalysts from Engelhard based on copper oxide−copper chromite have been employed. The properties of the catalysts are given in Table 1. The catalysts were boiled for 4 h in distillated water at pH 3.5 before being placed in the fixed-bed reactor.

Experimental Setups. The experimental setups and procedures for cyclohexanol dehydrogenation and Beckmann rearrangement are described below.

Dehydrogenation of a Cyclohexanol. Dehydrogenation of a cyclohexanol was carried out at atmospheric pressure in a fixed-bed reactor (FBR) made of a stainless-steal tube with 0.85-cm internal diameter and 25-cm length. The entrance of the reactor was filled with a small length (about 2 cm) of nonporous glass pellets of 1 mm. Over this, a bed of 10 g of catalyst pellets crushed to 1 mm in diameter, diluted with glass particles as mentioned above, was placed. The reactor was located in an oven with a PID temperature controller (±1K). Two different preheaters were used for the gas (N_2 as inert gas) and vaporized liquid (cyclohexanol) lines to reach the operational conditions. The cyclohexanol liquid flow rate was changed from 22 to 140 mL/h (W/F_{CHLo} from 47.8 to 7.5 g_{CAT} h/$mol_{Cyclohexanol}$) and the nitrogen flow rate was set to maintain a molar fraction of cyclohexanol of about 0.8 at the reactor entrance. The vapor effluent from the reactor was cooled at 25 °C, gas ($N_2 + H_2$) and liquid phase were separated, and liquid samples were collected for further analysis. A detailed scheme of the experimental FBR setup is given in Figure 1. The cyclohexanol fed to the reactor was purchased from Aldrich. In some runs 1-, 2-, and 3-methylcyclopentanol from Aldrich were added as cyclohexanol impurities.

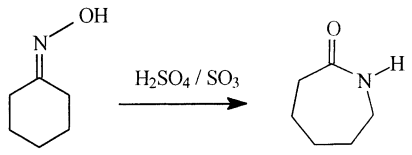
Purification of the reaction mixture was carried out to obtain cyclohexanone by rectification.

Oximation of Cyclohexanone. Next, the oximation of cyclohexanone with hydroxylamine sulfate (HAS) to obtain the cyclohexanone-oxime (CHN−Ox) was carried out. Cyclohexanone reagent was that obtained from dehydrogenation after separation from nonreacted cyclohexanol.



This reaction was carried out in a semibatch operation. About 200 g of an aqueous solution 45% in weight of HAS was thermostated at 85 °C in a 500-mL three-necked glass flask. The pH of this solution was set to 4.5 by adding a 20% aqueous solution of NH_3. Next, 100 mL of cyclohexanone was fed to the flask at a liquid flow rate of about 0.8 mL/min and the pH was set between 3.5 and 4.5 by adding the aqueous 20% NH_3 solution when necessary. The reaction temperature was maintained at 85 ± 1 °C. After the addition of the 100 mL of cyclohexanone, 10 g of the hydroxylamine sulfate solution was added as a reactant excess, and the reaction media was maintained for 45 min at 85 °C for cyclohexanone quantitative consumption. Organic and aqueous phases are separated in a preheated glass funnel and organic phase (cyclohexanone-oxime and organic impurities) is recovered for the next reaction step. A sample of this organic phase is analyzed by CG/MS.

Afterward, the Beckmann rearrangement of cyclohexanone-oxime above obtained to ϵ-caprolactam was carried out in sulfuric acid media.



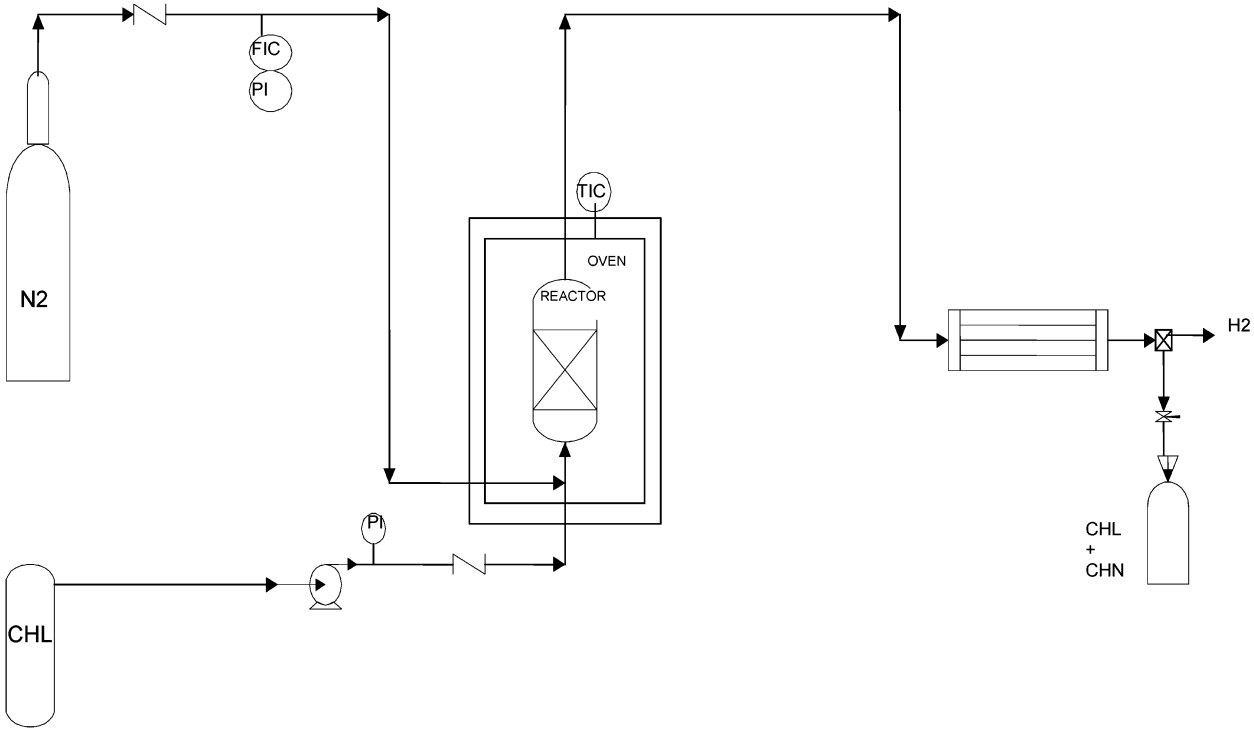


Figure 1. Experimental setup for cyclohexanol dehydrogenation.

This reaction was done in a semibatch manner by adding slowly 50 g of cyclohexanone-oxime over 250 mL of H_2SO_4 (96%, w/w) and thermostated at 75 °C in a 500-mL glass flask. After addition of cyclohexanone-oxime, the reaction medium was maintained for 60 min at 75 °C in the flask. The flask was closed during the reaction to increase the SO_3 content. After this time the flask was cooled to room temperature and a sample of 3 mL of the reaction media was neutralized with 9 mL of aqueous NH_3 (30% v/v). The organic phase was extracted with three aliquots of 3 mL of benzene. Next, distillated water was added to the remaining solid (ammonium sulfate) and aqueous phase until total dissolution of the solid. The final aqueous phase obtained was extracted with three aliquots of 20 mL of benzene. Organic and aqueous phase were analyzed by GC/MS.

Analytical Methods

Products and impurities of the cyclohexanol dehydrogenation have been analyzed by GC/MS (HP6890 GC-MS, detector MSD 5973). A HP-INNOWAX (cross-linked PEG) 30 m × 0.25 mm × 0.25 μm column has been used for the impurities with a molecular mass higher than cyclohexanol at the following conditions (method 1): carrier gas, helium, 1.8 mL/min, T_{injector} = 230 °C, T_{detector} = 250 °C, oven T_o = 60 °C, 1 min, rate 2 °C/min, T_1 = 77 °C, 3 min, rate = 20 °C/min, T_2 = 190 °C, 10 min, split 40:1. For the impurities such as cyclohexanol or lighter, a DB1 J&SCIENTIFIC (polydimethyl siloxane) 30 m × 0.25 mm × 1 μm column has been used at the following conditions (method 2): carrier gas, helium, 1 mL/min, T_{injector} = 230 °C, T_{detector} = 250 °C, split 25:1, oven temperature 50 °C for 30 min. One microliter of sample was injected in all cases.

Products and impurities of the cyclohexanone oximation and Beckmann rearrangement reaction have been analyzed by GC/MS (HP6890 GC-MS, detector MSD 5973) by using the DB1 J&SCIENTIFIC column described above. Analysis conditions were (method 3): carrier gas, helium, 1 mL/min, T_{injector} = 280 °C, T_{detector} = 230 °C, split 25,1:1, oven temperature T_o = 100 °C, rate 10 °C/min, T_1 = 280 °C, 1 min. One microliter of sample was injected. The cyclohexanone oxime solid obtained after oximation was dissolved in benzene (1 g of oxime diluted in 88 g of benzene). The organic phase reached after neutralization and extraction with benzene of organic and aqueous phases (by the procedure cited above) of the sample obtained after Beckmann rearrangement was analyzed by GC/MS (method 3). However, it is known that ϵ-caprolactam is quite soluble in water, and thus a high solubility for δ-valerolactams in water also can be inferred. Nevertheless, the analysis of the final aqueous phase causes difficulties because the ammonium sulfate in the final aqueous phase of sample obtained after Beckmann rearrangement produces a big noise in the GC/MS chromatograms. Therefore, to fit the mass balance for ϵ-caprolactam and methyl-δ-valerolactams, the relative solubilities of both in benzene and water have been obtained. To do this, ϵ-caprolactam from Aldrich was used. However, the 2-methyl-δ-valerolactam is not commercial and it was synthesized from 2-methylcyclopentanone by a procedure similar to that which follows for ϵ-caprolactam from cyclohexanone. The relative solubilities at 25 °C (defined as the ratio of ppm of compound in benzene and water when equilibrium is reached) obtained for ϵ-caprolactam and δ-valerolactams are 0.8 and 0.5, respectively. Therefore, it is concluded that these compounds are more soluble in water than in benzene.

All standards used for quantitative analysis were purchased from Sigma-Aldrich. Cyclohexanone-oxime, methylcyclopentanone oximes, and methyl-δ-valerolactams are not commercial products and were synthesized for this work.

Table 2. Experimental Runs for Cyclohexanol Dehydrogenation[a]

compound	catalyst 1 Cu-0203 T				catalyst 2 Cu-1230	
run	**1**	**2**	**3A/3B**	**4**	**5**	**6**
***T* (°C)**	**250**	**250**	**250/270**	**250**	**250**	**270**
W/F_{CHL_0} (g/h·mol)	47.85	27.7	15.25	7.5	15.25	15.25
XCHL	0.55	0.45	0.33/0.41	0.085	0.38	0.49
RCHN	0.96	0.98	0.96/0.98	0.94	0.97	0.92
CHE	12423	7679	5010/6101	1944	11762	10225
1,2,3-MeCPL	0	0	0	0	0	0
2,3-MeCPN	0	0	0/0	0	0	0
1-MeCPE	−	−	−/417	−	0	0
2-CHEL	36	51	59/23	16	37	18
3-CHEL	114	119	130/204	373	215	140
DCH ether	1995	1292	807/755	427	506	381
PhOH	1434	636	380/492	228	1355	2743
CHCHN	3306	1643	836/347	95	3456	10640
CHCHE	465	152	79/29	17	37	136
CHBz	3439	2299	2831/5547	1662	3288	3841
CHPhOH	9	0	0/0	95	0	0
2-CHEN	1610	1520	1140/1065	1168	945	1090
2-PhPhOH	85	66	47/0	24	21	17
CHCHEN	11571	4883	3429/4790	905	4822	13598
DCHE	361	133	32/51	0	353	1382

[a] $P = 1$ bar. $Y_{CHL_0} = 0.8$ (impurities of CHL_0 are dicyclohexyl ether = 266 (CR), 2-cyclohexen-1-ol = 1832 (CR), and 3-cyclohexen-1-ol = 624 (CR).

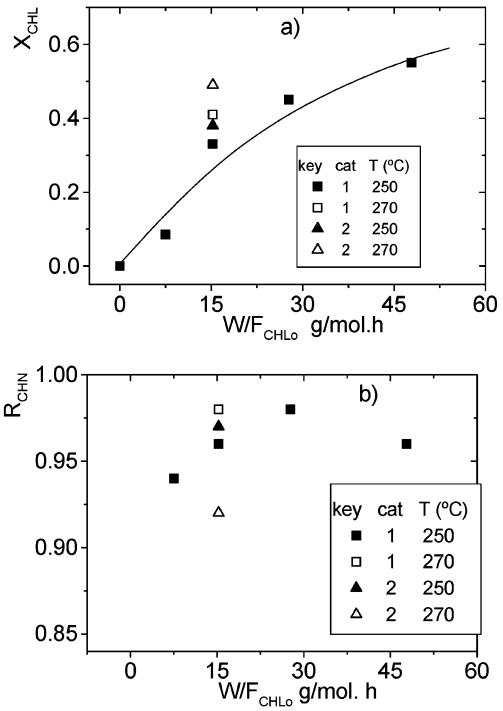


Figure 2. Cyclohexanol dehydrogenation with catalyst 1. $y_{CHL_0} = 0.8$, $P = 1$ bar. (a) Cyclohexanol conversion vs W/F_{CHL_0}. (b) Yield to cyclohexanone vs W/F_{CHL_0}.

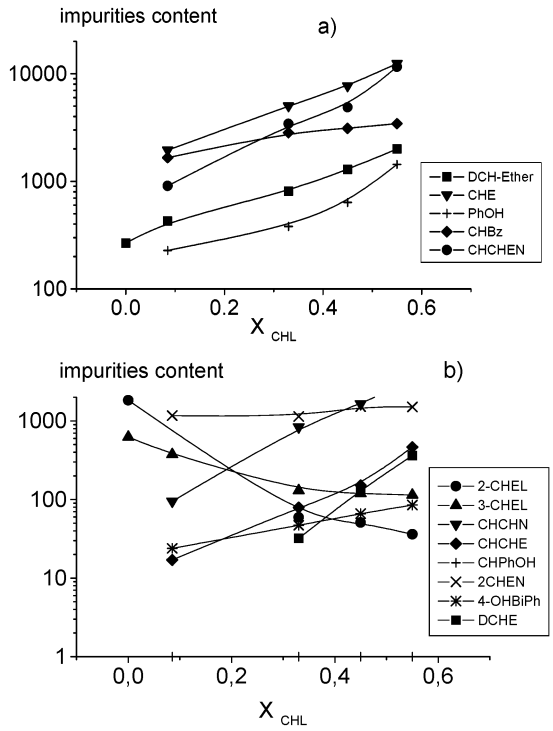


Figure 3. Impurities change with cyclohexanol conversion. Catalyst 1. $y_{CHL_0} = 0.8$, $P = 1$ bar. Catalyst 1. $T = 250$ °C. (a) Mayor impurities. (b) Minor impurities.

Results and Discussions

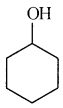
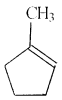
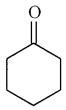
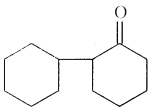
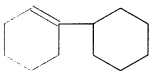
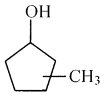
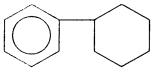
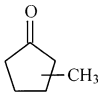
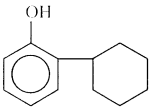
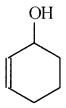
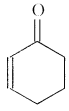
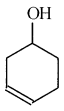
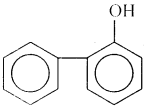
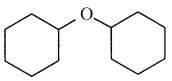
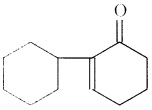
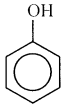
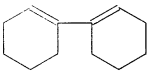
Dehydrogenation of Cyclohexanol. Experimental runs by feeding cyclohexanol from Aldrich to the FBR are summarized in Table 2. Only 2- and 3-cyclohexenols and dicyclohexyl ether were found as impurities in the reactant. It was found that neither methylcyclopentanones nor methylcyclopentene are obtained in runs given in Table 2. In Figure 2 the comparison for cyclohexanol conversion and cyclohexanone yield obtained for the two catalysts employed is given. The cyclohexanol to cyclohexanone yield is defined as

$$R_{CHN} = \frac{m_{CHN}}{m_{CHL_0} X_{CHL}}$$

Here, m is the mass of the compound and X the conversion. Subscript "0" is related to the initial amount.

In Table 2 is also given the distribution products obtained with cyclohexanol conversion and temperature, for both catalysts used. In Figure 3a,b the change in impurities content with cyclohexanol conversion is shown for catalyst 1 at 250 °C. In Table 3 are given the abbreviations and the molecular formulas of the reactant, main product, and impurities in the figures above. Only cyclohexanone and cyclohexene were quantitatively measured by calibration with standards and their impurities contents are given as mg/kg of CHL_0. The rest of the compounds in Table 2 and Figure 3 are given as chromatographic response (CR = compound area/

Table 3. Nomenclature, Abbreviations, and Molecular Structures of the Impurities Found in the Dehydrogenation of Cyclohexanol and Methylcyclopentanols

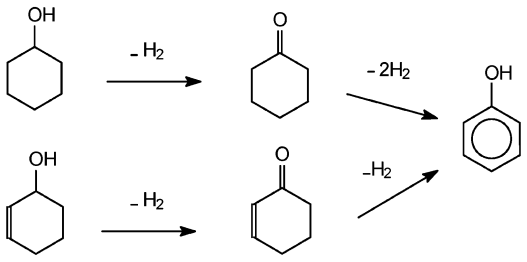
Nomenclature	MOLECULAR STRUCTURE	Nomenclature	MOLECULAR STRUCTURE
Cyclohexanol (CHL)		1-Methylcyclopentene (MeCPE)	
Cyclohexanone (CHN)		2-(Cyclohexyl) cyclohexanone (CHCHN)	
Cyclohexeno (CHE)		Cyclohexen-1-yl-Cyclohexane (CHCHE)	
2- and 3- Methylcyclopentanol (MeCPL)		Cyclohexylbenzene (CHBz)	
2- and 3- Methylcyclopentanone (MeCPN)		2-(Cyclohexyl)phenol (CHPhOH)	
2-Cyclohexen-1-ol (2-CHEL)		2-Cyclohexen-1-ona (2-CHEN)	
3-Cyclohexen-1-ol (3-CHEL)		2-Phenylphenol (2-PhPhOH)	
Dicyclohexyl ether (DCH Ether)		2-Cyclohexyl-2-cyclohexen-1-one (CHCHEN)	
Phenol (PhOH)		1-(Cyclohexen-1-yl) cyclohexene (DCHE)	

CHL_o area $\times 10^6$). CHL_0 is the value corresponding to $X_{CHL}= 0$. The mass balance of cyclohexanol reacted is quite adequately fit with the main product (cyclohexanone) and impurities obtained in the cyclohexanol dehydrogenation.

The reaction of cyclohexanol catalyzed by metals and metal ions on a variety of supports has been widely studied. It is well-known that cyclohexanol undergoes dehydrogenation not only on the C−O bond to give cyclohexanone but also in the cyclohexane ring to yield phenol. The route for cyclohexanol and the cyclohexenol impurity dehydrogenation are shown in Scheme 1. Cyclohexanol yields cyclohexanone and probably cyclohexenol produces cyclohexenone. A lower formation production of phenol has been observed in the reaction. Particularly, runs carried out with catalyst C1 yielded a negligible formation of phenol.

The catalyst (acid sites specially) can also produce the dehydration of cyclohexanol to cyclohexene (Scheme 2), and simultaneously, some dicyclohexyl derivatives products are produced by dehydration of cyclohexanol and

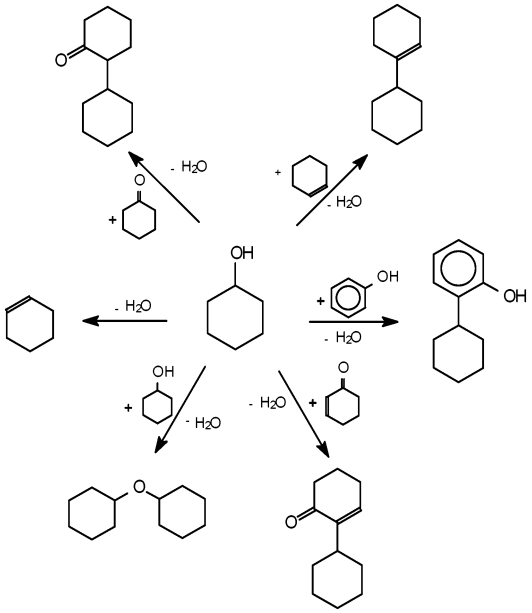
Scheme 1. Reaction Route of Cyclohexanol and Cyclohexenol Dehydrogenation



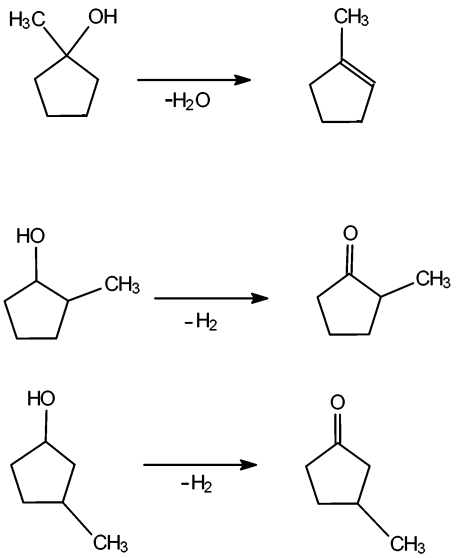
condensation with cyclohexanone, cyclohexene, phenol, cyclohexenone, and cyclohexanol. The routes to obtain dicyclohexyl derivatives products are summarized in Scheme 2.

Other generated impurities such as 1-(cyclohexen-1-yl)-cyclohexene and cyclohexylbenzene can be explained by the dehydrogenation reaction from cyclohexen-1-yl-

Scheme 2. Reaction Routes of Cyclohexanol Dehydration and By-products Obtained



Scheme 3. Transformation of Methylcyclopentanols



cyclohexane and also 2-phenylphenol is probably obtained from dehydration−condensation reaction of phenol.

When the catalyst C1 is used, the reaction is operated at a temperature of 250 °C and conversions of cyclohexanol between 0.20 and 0.30. Cyclohexene (CHE), 2-cyclohexyl-2-cyclohexen-1-ona (CHCHEN), cyclohexylbenzene (CHBz), and 2-cyclohexenone (CHEN) are the only impurities formed from the reactants and products (independently of the impurities of the feeding) that can overcome the 1000 ppm. Phenol and 2-cyclohexylcyclohexanone (CHCHN) also overcome this limit concentration when catalyst C2 is used.

Because no methylcyclopentanones and no methylcyclopentene are obtained when no methylcyclopentanols are fed, it can be supposed that the methylcyclopentanone may be produced from methylcyclopentanols and not from cyclohexanol dehydrogenation. Methylcyclopentanones can react in the oximation and

Table 4. Experimental Runs for Cyclohexanol + Methylcyclopentanols Dehydrogenation[a]

			ppm$_0$ (mg/kg of CHL$_0$)				
run	T (°C)	cat	1-MeCPL	2-MeCPL	3-MeCPL	X_{CHL}	R_{CHN}
7	250	1	220	0	0	0.33	0.91
8	250	1	0	1565	0	0.33	0.97
9	250	1	0	0	1514	0.33	0.91
10	250	1	906	750	325	0.33	0.97
13	270	1	980	1042	1038	0.41	0.98
15	250	2	973	994	995	0.38	0.97
16	270	2	973	994	995	0.49	0.92

[a] $P = 1$ bar. Y_{CHL_0}=0.8. $W/F_{CHL_0} = 15.25$ g of cat·h/mol.

Beckmann rearrangement steps, yielding finally δ-valerolactam. These last are typical impurities of ϵ-caprolactam when cyclohexanol is obtained from benzene partial hydrogenation followed by hydration. To study how methylcyclopentanones are formed from methylcyclopentanols, some additional runs, summarized in Table 4, have been carried out by adding these last compounds as cyclohexanol impurities. Methylcyclopentanols have been added separately (runs 7, 8, and 9) and together (runs 10, 11, 12, and 13). Apart from the impurities described in Table 2 and Scheme 3, only 2-, 3-methylcyclopentanones and 1-methylcyclopentene are obtained. All these compounds, and the methylcyclopentanols added as impurities, have been quantified by GC/MS by using standards and their amounts have been calculated as ppm (mg of compound/kg of CHL$_0$). Cyclohexanol conversion and cyclohexanone yield are also given in Table 4. Results obtained from runs in Table 4 are shown in Figure 4.

For run 7 it was found that 1-methylcyclopentanol is not dehydrogenated but only dehydrated to 1-methylcyclopentene. From runs 8 and 9 it was observed that the 2- and 3-methylcyclopentanols give quantitatively the 2- and 3-methylcyclopentanones, respectively. When the three methylcyclopentanols are added together (run 10), the results obtained are consistent with those found for runs 7, 8, and 9. Conversion of 1-methylcyclopentanol is almost negligible and the 3-methylcyclopentanol dehydrogenates significantly faster than 2-methylcyclopentanol and with a yield near to 1- to 3-methylcyclopentanone. This fact is not related to the thermodynamics because both 2- and 3-methylcyclopentanol have an equilibrium conversion at the conditions employed near unity. The yield value shown in Figure 4a is defined as

$$R_j = \frac{m_j}{m_{x-\mathrm{MeCPL}_0} X_{x-\mathrm{MeCPL}_0}}$$

being j = 2-methylcyclopentanone and 3-methylcyclopentanone for $x = 2, 3$, respectively.

In Figure 4b results obtained with catalyst 1 at 250 and 270 °C are shown. It can be seen that conversion for 1-methylcyclopentanol is notably increased when the temperature increases but only a slight increment is observed for 2- and 3-methylcyclopentanols. In Figure 5a the influence of temperature in the results obtained with catalyst 2 are shown. The temperature has a small influence for the conversion obtained with the three methylcyclopentanols. Both the conversion of 1-methylcyclopentanol and the amount of 1-methylcyclopentene are higher for catalyst 2 than for catalyst 1. This could be due to the dehydration effect of the alumina in catalyst 2.

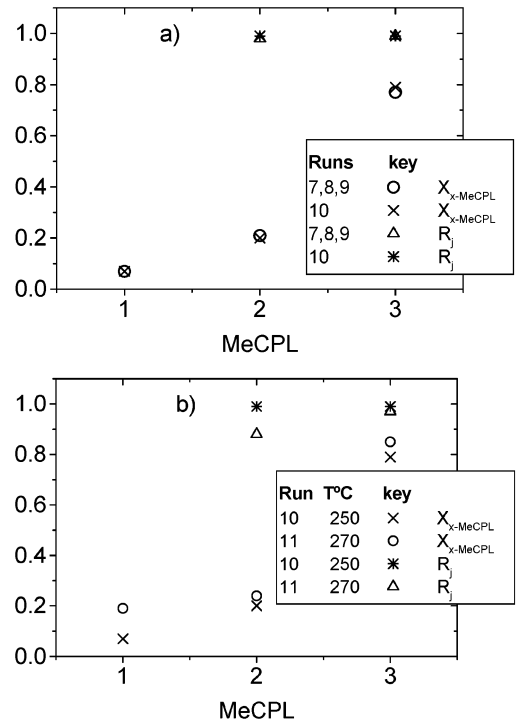


Figure 4. *x*-Methylcyclopentanol conversion and yield to *x*-methylcyclopentanone with catalyst 1. (x = 1, 2, 3). W/F_{CHL_0} = 15.25 g/mol·h, y_{CH_0} = 0.8, P = 1 bar. (a) T = 250 °C. *x*-Methylcyclopentanol mixed or not. (b) Influence of temperature

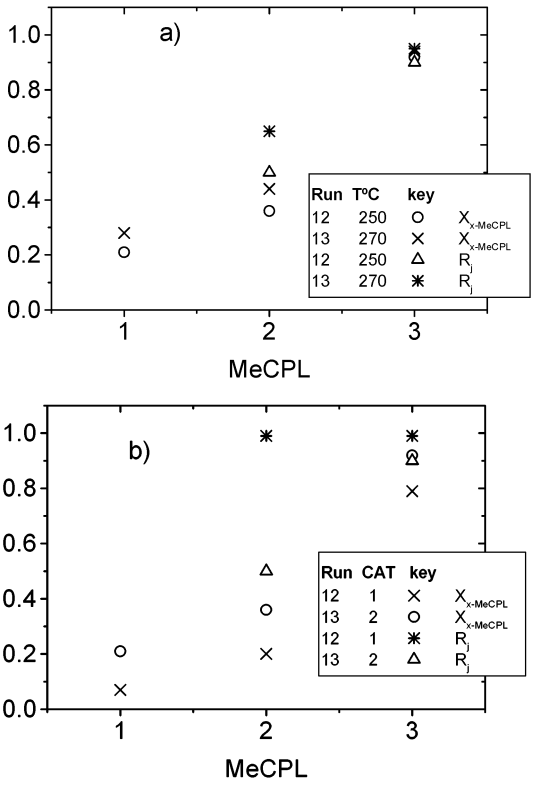


Figure 5. *x*-Methylcyclopentanol conversion and yield to *x*-methylcyclopentanone. W/F_{CHL_0} = 15.25 g/mol·h, y_{CHL_0} = 0.8, P = 1 bar. (a) Influence of temperature. Catalyst 2. (b) Influence of catalyst. T = 250 °C.

In Figure 5b a comparison of results obtained with catalysts 1 and 2 is shown. Catalyst 2 gives a higher conversion for the three methylcyclopentanols that is reached but with a lower yield that that of the corresponding methylcyclopentanones.

The selectivity is clearly observed in the transformations of cycloalkyl alcohols to cycloalkyl ketones. The isomerization does not take place from cyclohexanol/cyclohexanone to methylcyclopentanols/methylcyclopentanones (MeCPLs/MeCPNs). Moreover, the methylcyclopentanones of the cyclohexanol comes from selective dehydrogenation on the C−O bond of the corresponding methylcyclopentanols, under experimental conditions. However, a dehydration process takes place on the 1-methylcyclopentanol to give methylcyclopentene because it is not possible to dehydrogenate on the C−O bond of the 1-methylcyclopentanol to obtain the corresponding cyclopentanone. The order of the conversions rates is very similar for each catalyst and it is independent of the temperature of the process.

$$\text{Catalyst C1: } X_{3\text{-mecpl}} > X_{CHL} > X_{2\text{-mecpl}} > X_{1\text{-mecpl}}$$

$$\text{Catalyst C2: } X_{3\text{-mecpl}} > X_{2\text{-mecpl}} > X_{CHL} > X_{1\text{-mecpl}}$$

Conditions of Run 10 in Table 4 were selected to carry on with the cyclohexanone oximation and Beckmann rearrangement steps. A sufficient amount of cyclohexanol with the methylcyclopentanols impurities content of run 10 in Table 4 was fed to the reactor at steady-state conditions and the cyclohexanone was separated from cyclohexanol unreacted by rectification as described in the Experimental Section. The cyclohexanone composition, obtained after this separation−rectification step, is shown in Table 5. As can be seen, only 2- and 3-methylcyclopentanones and cyclohexanol are remaining as impurities on cyclohexanone. Therefore, the reactions of these impurities during cyclohexanone oximation and Beckmann rearrangement will produce the main impurities of ϵ-caprolactam obtained from benzene as raw material.

Table 5. Cyclohexanone Composition Obtained after Separation of Cyclohexanone from Cyclohexanol Dehydrogenated in Run 10 and Rectification of Cyclohexanone

compound	pm (mg/kg of CHN)
CHL	−
1-MeCPL	1020
2-MeCPN	283
3-MeCPN	579

Table 6. Results Obtained after Cyclohexanone Oximation

impurity	X	ppm (mg/kg·CHN oxime)	ppm (mg/kg·CHN_0)
CHN	CHN = 0.998	1703	1958
1-MeCPL	1-MeCPL = 0	920	1058
2-MCPN-oxime	2-MeCPN = 100	283	325
3-MCPN-oxime	3-MeCPN = 110	695	799

Cyclohexanone Oximation and Beckmann Rearrangement. Cyclohexanone oximation was carried out in a semibatch manner following the procedure described in the Experimental Section. The conversion of cyclohexanone and 2- and 3-methylcyclopentanones was almost complete (X_{CHN} = 0.998) and reacted quantitatively to the corresponding oximes but 1-methylcyclopentanol does not react. Results obtained are summarized in Table 6. The impurities contents are both given in relation to the cyclohexanone-oxime and initial

Table 7. Results Obtained after Cyclohexanone-Oxime Beckmann Rearrangement

impurity	ppm (mg/kg·oxime)
CHN-oxime	120
1-MeCPL	traces (<20 ppm)
methyl-δ-valerolactame	1200

cyclohexanone, taking into account the molecular weights of cyclohexanone and cyclohexanone-oxime.

The **Beckmann** rearrangement of the cyclohexanone-oxime with the impurities in Table 6 was carried out as previously described. After this reaction three phases were obtained, one solid corresponding to the ammonium sulfate, a second organic phase, and an aqueous phase. By means of the procedure described in the Analytical Section, the values of ϵ-caprolactam and impurities contained in all these phases were calculated. Results are summarized in Table 7. As can be seen, the cyclohexanone-oxime reacts almost quantitatively. The ϵ-caprolactam obtained (sum of those contained in the three phases) corresponded to the cyclohexanone-oxime reacted. The 1-methylcyclopentanol content in the cyclohexanone-oxime is drastically reduced (probably a dehydration followed by evaporation of the 1-methylcyclopentene has taken place in the hot sulfuric media). The methylcyclopentanone-oximes react quantitatively to the δ-valerolactams. An error of about 20% has been obtained. This error can be due to an experimental error in the relative solubilities of δ-valerolactam in aqueous and organic phase determination and/or an error in the analytical method.

Conclusions

Methylcyclopentanones in the cyclohexanone come exclusively from the dehydrogenation of methylcyclopentanols as impurities of cyclohexanol. Neither is it possible to obtain methylcyclopentanols from cyclohexanol in the process.

Whatever catalyst that is used, the reaction of each methylcyclopentanol takes place in a different way to obtain three different products. Therefore, the methylcyclopentanols composition of cyclohexanol and the methylcyclopentanols transformations are very important aspects of exercising control on the methylcyclopentanones composition in cyclohexanone and so on the methyl-δ-valerolactams composition in the final ϵ-caprolactam.

Transformations of cyclohexanone and 2- and 3-methylcyclopentanones in cyclohexanone-oxime and 2- and 3-methylcyclopentanones-oximes and the subsequent ϵ-caprolactam and 3-, 4-, 5-, and 6-methyl-δ-valerolactams are almost quantitative. It gives special value to know the unequivocal transformation route of methylcyclopentanols.

Acknowledgment

This work has been supported by Asahi Chemical Industry Co., Ltd. and by Spanish MCT under Contract DGES PB98-0839. The authors wish to thank Asahi Chemical Industry Co. for permission to submit this paper for publication.

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Received for review December 11, 2002
Revised manuscript received May 30, 2003
Accepted June 2, 2003

IE0210154