VAPOR-PHASE HYDRATION OF PROPYLENE OXIDE OVER TRICALCIUM PHOSPHATE

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Tricalcium phosphate is an active stable and specific catalyst for hydrolysis, hydration, and dehydration. It was recently established that it also catalyzes the hydrolytic cleavage of mesityl oxide to acetone [1] and cyclohexylidenecyclohexanone-2 to cyclohexanone [2]. It may be conjectured that the activity of the phosphate in processes of an acid-base nature may be caused by its weakly acidic properties [3].

The catalytic properties of calcium phosphate in the hydration of propylene oxide were studied in the present work. A review of work on the hydration of organic oxides was given in the monograph of Curme and Johnston [4]. Ethylene oxide does not react with water vapor, even at 200° [5], but in the presence of the catalysts H^+ and OH^- ions it is hydrated even at room temperature. For industrial purposes ethylene oxide is hydrated in the liquid phase in the presence of mineral acids (for example, 0.5% sulfuric acid) at 50-70°. The glycol yield exceeds 90% of theoretical [4]. The reaction may also be carried out in the absence of catalysts in the liquid phase at 180-200° under pressure. A large excess of water (12-20-fold) is used to prevent the formation of polyglycols both in the presence of catalyst and without it. The latter circumstance, which involves a considerable consumption of heat in the isolation of the product, and also the difficulties arising during the additional, careful freeing of the reaction products from traces of acid, compels a search for new methods of carrying out this process. In particular, heterogeneous vapor-phase hydration is apparently a promising method. Little study has been devoted to the hydration of oxides on solid catalysts. The main difficulty in achieving the vapor-phase hydration of oxides is their tendency to isomerize into the corresponding aldehydes or ketones. In the hydration of ethylene oxide on silica gel, phosphoric acid on silica gel, or aluminum or thorium oxide over the temperature range of 153-167° with a molar ratio of water to oxide of 2 to 19, a water-aldehyde mixture was obtained and glycol was not detected in the reaction products [6]. Only silver oxide (8.7%) deposited on aluminum oxide catalyzed the hydration. At 150-210° the ethylene oxide conversion in one pass was 20-30%. After the catalyst had operated for 5-6 hr, its activity fell sharply due to blocking of its surface with tarry products. The catalyst did not recover its activity completely after treatment with superheated steam. Ion-exchange resins, both acid and basic, have been recommended as catalysts for ethylene oxide hydration. At 115°, a slight pressure, and a molar ratio of water : ethylene oxide of 10:1, the glycol yield was 80-85% [7].

The results of our work show that tricalcium phosphate is an active and selective catalyst for the hydration of oxides in the vapor phase.

EXPERIMENTAL

The experiments were carried out on the flow apparatus described previously [1]. The temperature in the catalyst bed was maintained with an accuracy of $\pm 1^{\circ}$. Into a Pyrex tube was placed 20 ml of calcium phosphate in the form of granules, 2×3 mm, obtained from calcium chloride and diammonium phosphate. After each experiment, the catalyst was regenerated with air for 2 hr at 400-450°. Propylene oxide and water in definite ratios were passed at a steady rate over the catalyst with the aid of an automatic doser and cut-out [8]. The injector of the doser from which the propylene oxide was introduced was cooled with ice. The ethylene oxide flow rate was determined with a rheometer.

Analysis of reaction products. In each experiment, 8.5 ml (7.1 g) of propylene oxide was normally passed through the catalyst. The reaction products were fractionated on a column with an efficiency of 20 theoretical plates. The unreacted oxide distilled at 33-35°. Then a broad fraction was collected at 45-90° and this probably contained allyl alcohol and propionaldehyde. For example, in an experiment at 232° with a molar ratio of water: propylene oxide of 12:1 and a contact time of 15.7 sec, we obtained 0.7 g of this fraction and the oxime method showed that it contained 11.6% of carbonyl-containing compound, calculated on propionaldehyde. Hydrogenation in the presence of Raney nickel catalyst at 20° showed that it contained 35.2% of unsaturated compound, calculated on allyl alcohol.

At 100° we collected a certain amount of pure water. A water-glycol mixture, containing 10-15% of glycols, remained in the still boiler. In separate experiments, when a sufficient amount of aqueous glycol solution had accumulated, it was distilled with the isolation of glycol. The glycol content of the aqueous solution was determined from the refractive index [4] as the catalyzate consisted only of water and glycols and the amount of di- and polyglycols did not exceed 15-20% of the total amount of glycols. In control experiments, satisfactory agreement was found between the amounts of propylene glycol isolated by fractionation and the amounts determined refractometrically.

The propylene oxide used in the experiments was first distilled over metallic sodium and had b.p. 34.0-34.5° (760 mm); n_D^{20} 1.3657; d_{20}^{20} 0.8306. Commercial ethylene oxide was used.

Effect of temperature, contact time, and the water : propylene oxide ratio. The effect of temperature on the degree of conversion of propylene oxide is shown in experiments 1-12 (table) and Fig. 1. The data presented show that over the temperature range $130-194^{\circ}$ (experiments 1-5) the glycol yield changed little. No by-products were present. When the temperature was raised to 260° , the glycol yield began to increase rapidly and at 232° it was 28% and at 260°, 40%. The formation of by-products forming the fraction with b.p. $45-90^{\circ}$ simultaneously became appreciable. With a decrease in the contact time (experiments 9 and 10) in the temperature range 190-230°, the glycol yield also changed little (from 9 to 14%), while in the temperature range 230-260°, it increased to 27%. With a further increase in temperature to 280° , the glycol yield changed insignificantly, but at the same time, up to 20% of by-products was formed.

Expt. No.	Temp, °C	Con- tact time, sec	H ₂ O : C ₃ H ₆ O molar ratio	C ₃ H ₈ O ₂ yield on oxide passed, %	Expt. No.	Temp, °C	Con- tact time, sec	H ₂ O : C ₃ H ₆ O molar ratio	C ₃ H ₈ O ₂ yield on oxide passed, %
1 2 3 4 5 6 7 8 9 10	$134 \\ 153 \\ 163 \\ 184 \\ 194 \\ 232 \\ 240 \\ 260 \\ 193 \\ 232$	9,4 9,4 9,4 9,4 9,4 9,4 9,4 9,4 9,4 9,4 9,4 9,4 4,7 4,7	$\begin{array}{c} 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \\ 6,8 : 1 \end{array}$	$ \begin{array}{c} 11\\ 14\\ 13\\ 15\\ 14\\ 28\\ 31\\ 40\\ 9\\ 14\\ \end{array} $	$ \begin{array}{c} 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \\ \end{array} $	$\begin{array}{c} 260\\ 280\\ 232\\ 232\\ 232\\ 232\\ 260\\ 260\\ 260\\ 260\\ 260\end{array}$	$\begin{array}{r} 4,7\\ 4,7\\ 3,1\\ 4,7\\ 9,4\\ 14,0\\ 4,7\\ 4,7\\ 4,7\\ 4,7\\ 4,7\\ 4,7\end{array}$	$\begin{array}{c} 6,8:1\\ 6,8:1\\ 6,8:1\\ 6,8:1\\ 6,8:1\\ 6,8:1\\ 3,3:1\\ 6,8:1\\ 3,3:1\\ 13,2:1\\ 19,7:1 \end{array}$	27 27 11 14 28 48 21 28 38 50

Effect of Temperature, Contact Time, and Water : Propylene Oxide Ratio on the Propylene Glycol Yield

The effect of contact times between 3.1 and 14.0 sec was studied. Experiments 13-16 and Fig. 2 show that at 232° and a molar ratio of water to propylene oxide of 6.8: 1, an almost linear relation was observed between the glycol yield and the contact time. At a contact time of 14.0 sec, the degree of conversion of oxide into glycol was 48%. However, with an increase in contact time, there was an increase in the formation of by-products and a decrease in the glycol yield on the oxide reacting.



Fig. 1. Effect of temperature on propylene glycol yield at contact times of $9.4 \sec(1)$ and $4.7 \sec(2)$.

Experiments 17-20 and Fig. 3 show that there is a linear relation between the propylene glycol yield and the molar ratio of water : propylene oxide. At 260°, a contact time of 4.7 sec, and a molar ratio of water : oxide of 19.7 : 1, the glycol yield reached 50%. In experiments 18-20 the glycol yield on the propylene oxide reacting was 90-93%. It is important that in the presence of a large excess of water not only did the glycol yield increase, but there was also a decrease in the formation of by-products (fraction with b.p. $45-90^{\circ}$).

Study of catalyst stability. Two long experiments were carried out to determine the stability of the catalyst in the process investigated. The water-glycol mixtures collected were distilled with the isolation of pure propylene glycol.

Experiment 21. Water and propylene oxide in a ratio of 6.4:1 were passed through 20 ml of catalyst at 232° with a contact time of 4.7 sec. A total of 115 ml of propylene oxide was passed. Over a period of 18 hrs operation without regeneration of the catalyst, there were no appreciable changes in the activity of the catalyst and the propylene glycol yield, determined every 2 hr, varied over the range 12.5-15.5%.



Fig. 2. Effect of contact time on propylene glycol yield.



Fig. 3. Effect of the molar ratio of water : propylene oxide on propylene glycol yield.

Experiment 22. In 14 hours operation without regeneration, 42.5 ml of propylene oxide was passed over 60 ml of catalyst at 232° with a contact time of 9.4 sec and a molar ratio of water : propylene oxide of 19.7:1. Control analyses were carried out after every 2 hr. The propylene glycol yield was 50-57%.

When a mixture of oxide, water, and glycol was passed under analogous conditions, the catalyst activity fell rapidly, but was recovered after regeneration. When the products collected in experiments 21 and 22 were distilled at 10 mm, two fractions were collected: Fraction I,with b.p. 80-83°, consisted mainly of propylene gly-col, and fraction II, with b.p. 90-108°, was mainly dipropylene glycol. In experiment 21, di- and polyglycols formed 15% of the total amount of glycol, and, in experiment 22, 17%. Approximately 5% of low-boiling prod-ucts (45-90°) was formed in the latter experiment.

Hydration of ethylene oxide. Experiments were also carried out on the hydration of ethylene oxide. The ethylene glycol content of the catalyzates was determined refractometrically. At 232°, a molar ratio of water : ethylene oxide of 12.4 : 1, and a contact time of 10.1 sec, the ethylene glycol yield was 37.0%. The acetalde-hyde yield represented 1.6-1.7% on the oxide passed.

EXPERIMENTAL RESULTS

It was established in [9] that the hydration of ethylene oxide in the liquid phase, catalyzed by H⁺ ions, proceeds by the mechanism

$$CH_2 - CH_2 + H^+ \rightleftharpoons CH_2 - CH_2;$$
(1)

$$CH_2 \rightarrow +CH_2 \rightarrow +CH_2 -CH_2OH;$$
 (2)

$$^{+}CH_{2}-CH_{2}OH + H_{2}O \rightleftharpoons CH_{2}OH - CH_{2}OH + H^{+}.$$
(3)

Stage (2) is the slowest. The formation of polyglycols also proceeds through the oxonium complex:

$$+CH_2-CH_2OH + CH_2OH - CH_2OH \neq CH_2OHCH_2OCH_2CH_2OH + H^+.$$

It is probable that vapor-phase hydration of ethylene oxide catalyzed by ion-exchange resins also proceeds by the same mechanism [10]. A completely different mechanism was proposed for vapor-phase hydration of ethylene oxide on a solid catalyst, silver oxide on aluminum oxide [6]. The catalytic action of the silver oxide was explained by activation of the water molecule:

$$Ag_2O + H_2O(gas) = Ag_2O(H_2O)...$$
 (1)

The complex formed reacts with an unactivated oxide molecule:

$$Ag_2O(H_2O) + C_2H_4O = (CH_2OH - CH_2OH) Ag_2O.$$
 (2)

Then follows the slowest stage of the process, namely, desorption of the glycol formed

$$(CH_2OH-CH_2OH) Ag_2O \rightarrow CH_2OH-CH_2OH(gas) + Ag_2O$$
(3)

and regeneration of the catalyst. However, if activation of the organic component of the reaction on this catalyst is not obligatory, then the route by which aldehyde is formed in the process remains incomprehensible.

The data obtained in our work indicate that hydration of oxides in the presence of calcium phosphate proceeds by the same mechanism as in the liquid phase in the presence of H^+ ions. This is confirmed by the linear relation of glycol yield to contact time and is in accord with the behavior of the phosphate catalyst in other hydrolysis and hydration processes.

In the vapor-phase hydration of oxides on solid catalysts there are a number of peculiarities, which are con nected with the different adsorbabilities of water, the starting oxide, and the glycols formed. In particular, this may explain the slow increase in the yield of glycol on calcium phosphate with a rise in temperature over a definite range and also the direct relation between the glycol yield and the water excess. It is probable that a rise in temperature and an increase in the water excess accelerate the desorption of glycols blocking the catalyst surface. The high specificity of calcium phosphate in hydration reactions gives grounds for assuming that isomerization of the oxide, which proceeds readily on other catalysts, is hindered on this catalyst. The experiments confirmed this. Thus, when propylene oxide was passed over the catalyst in the absence of water at 210° with a contact time of 7 sec, less than 1% of allyl alcohol and propionaldehyde was formed and at 280°, 8%. Allyl alcohol was completely unchanged on this catalyst at 230° and only 4% was isomerized to aldehyde at 320°.

It seemed interesting to compare the results of the present work with those obtained on other catalysts under similar temperature conditions. When a basic catalyst, namely, lithium phosphate, was used, propylene oxide was readily isomerized to allyl alcohol and propionaldehyde in the absence of water [11]. In experiments with phosphoric acid on silica gel, ethylene oxide only underwent isomerization and was not hydrated. Hydration proceeded selectively in the presence of sulfuric acid, silver oxide, ion-exchange resin, and calcium phosphate. The phosphate catalyst was better than the silver oxide in selectivity, stability, and regeneration. The stability and specificity of the phosphate catalyst may make it possible to use it in practice. In this case, it would be advantageous to use a continuous process with condensation of the high-boiling glycol and return of the unreacted oxide and water vapor to the reaction. 1. The catalytic activity of tricalcium phosphate in the vapor-phase hydration of propylene oxide to propylene glycol was studied.

2. Calcium phosphate is a stable and selective catalyst for this reaction.

3. The effect of temperature, contact time, and water excess on the glycol yield was studied. Considerable amounts of glycol were formed under the optimal conditions and the glycol yield reached 50-57% at 232°, for example similar results were obtained in the hydration of ethylene oxide.

4. The high specificity of the phosphate catalyst in the hydration of propylene oxide is in accord with the fact that it hardly catalyzes the isomerization of oxide to allyl alcohol and propionaldehyde.

5. The reaction mechanism is discussed.

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