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PREPARATION OF LITHIUM PHOSPHATE CATALYSTS

FIELD OF THE INVENTION

The invention relates to lithium phosphate catalysts. More particularly, the invention relates to lithium phosphate catalysts that have increased activity for the isomerization of alkylene oxide to allylic alcohol.

BACKGROUND OF THE INVENTION

Lithium phosphate catalyst has been commercially used for the isomerization of propylene oxide to allyl alcohol. The catalyst was first disclosed in U. S. Pat. No. 2,426,264. The catalyst preparation involves precipitating a crude lithium phosphate from the mixture of an aqueous solution that contains phosphate ions and an aqueous solution that contains lithium ions. The crude precipitate is then washed with water and dried to form catalyst powder.

Methods for improving lithium phosphate catalysts are known. For example, U.S. Pat. No. 2,986,585 teaches the use of additional alkali metal hydroxides such as sodium hydroxide and potassium hydroxide during the precipitation of lithium phosphate. Although the function of the additional alkali metals in the lithium phosphate catalyst is not clear, the resultant catalyst has improved activity and selectivity for the alkylene oxide isomerization.

Allyl alcohol has been commercially used as an intermediate for the manufacture of 1,4-butanediol. See U.S. Pat. No. 6,426,437. It has also been increasingly used as a hydroxyl functional monomer in the polymer industry. For instance, allyl alcohol is used for making styrene-allyl alcohol copolymers (see U.S. Pat. No. 5,444,141) and hydroxyl acrylic resins (see U.S. Pat. No. 5,475,073).

It is apparent that improving the lithium phosphate catalyst is important to the industry. Ideally, the catalyst would have increased activity or productivity but would not incur increased cost.

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Preferably, the phosphate ion concentration is within the range of about 0.5 M to about 1.5 M. More preferably, the phosphate ion concentration is within the range of about 0.5 M to about 1.0 M. Suitable phosphate compounds include those which are soluble in water. Preferably, the phosphate compounds are selected from the group consisting of sodium phosphates, potassium phosphates, ammonium phosphates and mixtures thereof. Sodium phosphates and their hydrates are particularly preferred.

Preferably, the borate ion concentration is within the range of about 0.5 M to about 2.5 M. More preferably, the borate ion concentration is within the range of about 1.0 M to about 2.0 M.

Suitable borate compounds include those which are soluble in water. Preferably, the borate compounds are selected from the group consisting of boric acid, sodium borates, potassium borates, ammonium borates and mixtures thereof. Boric acid, sodium borates and their hydrates are particularly preferred.

Preferably, both the first and the second solutions are heated, prior to mixing, to a temperature within the range of about 45°C to about 95°C. More preferably, the solutions are heated to a temperature within the range of about 60°C to about 80°C. The mixing is performed preferably with rapid stirring. It can be performed in a reactor or any suitable containers.

The ratio of the first and the second solutions is not critical. Preferably, the molar ratio of lithium ion/phosphate ion in the mixture is within the range of about 1/1 to about 6/1. More preferably, the ratio is within the range of about 2/1 to about 4/1.

Upon mixing, a crude lithium phosphate precipitates. The precipitate is then isolated and is washed with water. Washing is important. I have found that while the crude lithium phosphate has little catalytic activity in the isomerization of alkylene oxides, over-washed catalyst has diminished activity. Preferably, washing is so controlled that the washed lithium phosphate contains desirable amounts of sodium and boron.

Slurry phase isomerization is preferred. In the slurry phase isomerization of propylene oxide, the lithium phosphate catalyst is suspended in a high-temperature oil and the vaporized propylene oxide passes through the catalyst slurry to form allyl alcohol. The propylene oxide conversion is usually used to evaluate the activity or efficiency of the catalyst, which is calculated by

$$\text{Conversion (\%)} = \frac{\text{Propylene oxide reacted, wt}}{\text{Propylene oxide fed, wt}} \times 100$$

Several side reactions compete with the desired isomerization, leading to the formation of by-products such as propionaldehyde, acetone, n-propanol and acrolein. Selectivity of allyl alcohol formation, which measures the purity of allyl alcohol before separation, is calculated by

$$\text{Selectivity (\%)} = \frac{\text{Allyl alcohol produced, wt}}{\text{Propylene oxide reacted, wt}} \times 100$$

Preferably, the isomerization of propylene oxide is performed at a temperature within the range of about 200°C to about 300°C. More preferably, the isomerization temperature is within the range of about 240°C to about 280°C. High isomerization temperature induces high catalyst activity. However, high temperature also decreases allyl alcohol selectivity. I have found that the catalyst of the invention maintains high activity at a relatively low isomerization temperature and therefore increases allyl alcohol selectivity without sacrificing the productivity.

The following examples further illustrate the invention. Examples 1 and 2 illustrate the preparation of the lithium phosphate catalysts that contain both sodium and boron. These catalysts give increased conversion of the isomerization of propylene oxide to allyl alcohol. In comparison, the catalysts in Comparative Examples 3 and 4, which do not contain either boron or sodium, show low propylene oxide conversion.

temperature of 10°C or lower. The bottom glass tube has a porous frit for the entrance of the propylene oxide which is introduced from an ISCO pump. The lithium phosphate catalyst slurry (7 g of catalyst in 65 g of Therminol™-55 heat transfer fluid (product of Solutia, Inc.)) is charged into the glass tube. Propylene oxide is vaporized in a preheating zone prior to its contact with the lithium phosphate catalyst. The reaction is performed at 273°C by continuously feeding propylene oxide at a rate of 20 cc per hour. Samples are periodically collected and analyzed by GC for the propylene oxide conversion and the product selectivity. The propylene oxide conversion is within the range of 53.5% to 59.2%. The allyl alcohol selectivity is within the range of 92.7% to 93.0%.

EXAMPLE 2

Lithium Phosphate Catalyst Containing both Sodium and Boron

The general procedure of Example 1 is repeated except in the first flask, 43.5 g of sodium phosphate dodecahydrate and 20 g of sodium tetraborate decahydrate are dissolved. The resultant lithium phosphate catalyst contains 0.1-0.3 wt % of sodium and 0.3-0.6 wt % of boron. The propylene oxide conversion is within the range of 54.0% to 58.7% and the allyl alcohol selectivity is within the range of 92.8% to 93.0%.

COMPARATIVE EXAMPLE 3

Lithium Phosphate Catalyst Containing Sodium but No Boron

The general procedure of Example 1 is repeated except in the first flask, 43.5 g of sodium phosphate dodecahydrate is dissolved in 150 ml of distilled water but no borate is used. The propylene oxide conversion is within the range of 41.0% to 43.8%. The allyl alcohol selectivity is within the range of 92.6% to 92.9%.

COMPARATIVE EXAMPLE 4

Lithium Phosphate Catalyst Containing Boron but No Sodium

The general procedure of Example 1 is repeated except in the first flask, 13.3 g of 85% phosphoric acid and 10 g of boric acid are dissolved in 150 ml of

EXAMPLE 7

Isomerization at Low Temperature with Lithium Phosphate Catalyst Containing both Sodium and Boron

The general procedure of Example 1 is repeated but the isomerization is performed at 253°C. The propylene oxide conversion is within the range of 39.9% to 42.5% and allyl alcohol selectivity within the range of 93.6% to 94%.

EXAMPLES 8-17 and Comparative Examples 18 and 19

The Effect of Boron and Sodium Concentrations on the Catalyst Activity and Allyl Alcohol Selectivity

The general procedure of Example 1 is repeated by varying the amounts of sodium phosphate, boric acid, lithium hydroxide and sodium hydroxide or varying the washing procedure to obtain lithium phosphate catalysts having different amounts of boron and sodium. These examples show the effects of the concentrations of boron and sodium and the ratios of boron/lithium and sodium/lithium on the isomerization of propylene oxide to allyl alcohol. The lithium, boron and sodium concentrations are measured by element analysis. The results are listed in Table 2.

TABLE 2

Effect of Boron and Sodium Concentrations on Isomerization of Propylene Oxide

Ex. No.	Sodium wt %	Sodium/lithium Molar Ratio	Boron wt %	Boron/lithium Molar Ratio	Propylene* Oxide Conversion	Allyl Alcohol* Selectivity
8	0.22	0.00374	0.42	0.0152	59.2%	93.0%
9	0.16	0.00271	0.34	0.0123	57.2%	92.7%
10	0.31	0.00528	0.54	0.0196	55.8%	93.0%
11	0.06	0.00102	0.59	0.0212	55.0%	92.4%
12	0.05	0.00085	0.43	0.0155	54.9%	92.5%
13	0.08	0.00136	0.29	0.0105	48.0%	92.4%
14	0.03	0.00051	0.20	0.0072	49.8%	92.1%
15	0.02	0.00034	0.32	0.0115	48.1%	92.0%
16	0.65	0.0111	0.65	0.0236	48.7%	92.6%
17	0.66	0.0113	0.85	0.0310	45.3%	92.4%
C18	1.7	0.0296	1.2	0.0444	20.8%	90.5%
C19	1.7	0.0297	1.4	0.0520	12.5%	91.1%

* Average value

12. A lithium phosphate catalyst which contains effective amounts of boron and sodium to enhance the catalyst activity and selectivity for an isomerization of alkylene oxide to allylic alcohol.

13. The catalyst of claim 12 which contains from 0.03 wt% to 1 wt% of boron.

14. The catalyst of claim 12 which contains from 0.1 wt% to 0.8 wt% of boron.

15. The catalyst of claim 12 which contains from 0.01 wt% to 1 wt% of sodium.

16. The catalyst of claim 12 which contains from 0.02 wt% to 0.8 wt% of sodium.

17. The catalyst of claim 12 which has a boron/lithium molar ratio within the range of 0.001 to 0.05.

18. The catalyst of claim 12 which has a boron/lithium molar ratio within the range of 0.003 to 0.03.

19. The catalyst of claim 12 which has a boron/lithium molar ratio within the range of 0.007 to 0.02.

20. The catalyst of claim 12 which has a sodium/lithium molar ratio within the range of 0.0002 to 0.02.

21. The catalyst of claim 12 which has a sodium/lithium molar ratio within the range of 0.003 to 0.01.

22. An isomerization process of propylene oxide to allyl alcohol in the presence of a lithium phosphate catalyst which contains effective amounts of boron and sodium.

23. The process of claim 22 which is performed in slurry phase.

24. The process of claim 22 which is performed at a temperature within the range of 200°C to 300°C.

25. The process of claim 22 which is performed at a temperature within the range of 240°C to 280°C.