Conference Paper

Mechanism of Allyl Alcohol Epoxidation with Hydrogen Peroxide at Titanium Catalyst (Ts-1)

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Abstract

Allyl alcohol epoxidation mechanism at the titanosilicate was studied. The best results were obtained for the hypothesis involving the hydrogen peroxide and allyl alcohol adsorption at the active catalyst centres with subsequent interaction of the surface intermediates with each other, with the formation of glycidol adsorbed on the active centre, free catalyst centre and molecule of water.

1. Scope

Oxygen-containing heterocyclic compounds (oxides olefins, cyclic acetals, etc.) are important products and intermediates of the basic and fine organic synthesis. Great practical interest is the glycidol oxide of allyl alcohol. It is a valuable intermediate product in the manufacture of surfactants, plasticizers, textile dyes, drugs, pesticides, some rubbers, paints, thermosetting resins and other [1].

2. Results and discussion

There are several basic methods for producing glycidol such as epoxidation of allyl alcohol with organic hydroperoxides at vanadium inorganic compounds as a catalysis; glycerol carbonate decomposition; chlorohydrins method; oxidation method; epoxidation of allyl alcohol with hydrogen peroxide [2].

One of the most promising methods for producing glycidol is the epoxidation of allyl alcohol by hydrogen peroxide on the titanium-containing catalyst.

\[
\text{CH}_3\text{OH}, 40^\circ\text{C}, 3\text{h} \xrightarrow{\text{H}_2\text{O}_2, \text{cat. TiO}_2\text{SiO}_2(\text{TS-1})} \text{CH}_3\text{OH, } 40^\circ\text{C}, 3\text{h} \xrightarrow{\text{H}_2\text{O}_2, \text{cat. TiO}_2\text{SiO}_2(\text{TS-1})} \text{CH}_3\text{OH, } 40^\circ\text{C}, 3\text{h} \xrightarrow{\text{H}_2\text{O}_2, \text{cat. TiO}_2\text{SiO}_2(\text{TS-1})} \]
Figure 1: The concentrations of allyl alcohol (a), hydrogen peroxide (b) and glycidol (c) in the course of a typical kinetic experiment.

Figure 2: The accordance between calculated and experimental concentrations of allyl alcohol (a), hydrogen peroxide (b) and glycidol (c) for all experiments (mechanism 14, table 1).

It was studied the epoxidation mechanism of allyl alcohol using titanosilicate zeolite (ts-1) at 40°C by means of procedures for the nomination and discrimination of mechanism hypotheses. The hypotheses were advanced on the basis of literature data and
Mechanism 1
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow C_H_6O_2 + H_2O + X_0
3 X_1 \rightarrow C_H_6O + H_2O + X_0

Mechanism 2
1 X + C_H_6O \rightleftharpoons X_1
2 X_1 + H_2O \rightarrow C_H_6O_2 + H_2O + X_0
3 X_1 \rightarrow C_H_6O + H_2O + X_0

Mechanism 3
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow C_H_6O_2 + H_2O + X_0
3 X_1 \rightarrow C_H_6O + H_2O + X_0
4 X_1 + H_2O \rightarrow C_H_6O_2 + H_2O + X_0

Mechanism 4
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 + X_2 \rightarrow C_H_6O_2 + H_2O + X_0

Mechanism 5
1 X + C_H_6O \rightleftharpoons X_1
2 X_1 + H_2O \rightarrow X_2
3 X_1 \rightarrow C_H_6O + H_2O + X_0

Mechanism 6
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 \rightarrow C_H_6O + H_2O + X_0
4 X_1 + H_2O \rightarrow X_2
5 X_1 + C_H_6O \rightarrow X_3

Mechanism 7
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 + C_H_6O \rightarrow C_H_6O_2 + H_2O + 2X_0

Mechanism 8
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 \rightarrow C_H_6O + H_2O + X_0

Mechanism 9
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 \rightarrow C_H_6O + H_2O + X_0

Mechanism 10
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 + C_H_6O \rightarrow C_H_6O_2 + H_2O + X_0

Mechanism 11
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 \rightarrow C_H_6O + H_2O + X_0

Mechanism 12
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 \rightarrow C_H_6O + H_2O + X_0
4 X_1 + C_H_6O \rightarrow X_3

Mechanism 13
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 + C_H_6O \rightarrow C_H_6O_2 + H_2O + X_0
4 X_1 + C_H_6O \rightarrow C_H_6O_2 + H_2O + X_0

Mechanism 14
1 X + H_2O \rightleftharpoons X_1
2 X_1 + C_H_6O \rightarrow X_2
3 X_1 + X_2 \rightarrow X_3 + H_2O + X_0
4 X_1 + C_H_6O \rightarrow C_H_6O_2 + X_0

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<th>Mechanism 13</th>
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Table 1: Hypothetical mechanisms for the allyl alcohol epoxidation.

For each hypothesis, it was formulated the corresponding system of differential equations and carried out the estimation of the rate constants. The quality of the experimental data description was judged by the residual sums of squared deviations and correlation coefficients. The most probable mechanism (14, table 1) involves the hydrogen peroxide and allyl alcohol adsorption at the catalyst active centers and the glycidol formation as adsorbed molecules of the reactants interaction via the reversible step.

the preliminary experiment results (table 1). Discrimination hypothetical mechanisms were carried out on the basis of the kinetic experiment results with varying concentrations of allyl alcohol, hydrogen peroxide and glycidol (Figure 1).
3. Conclusions

The best description of the results are obtained for the hypothesis involving the hydrogen peroxide and allyl alcohol adsorption at the two active catalyst centres with subsequent interaction of the surface intermediates with each other, with the formation of glycidol adsorbed on the active centre, free catalyst centre and molecule of water.

Acknowledgments

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References