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Experiments and kinetics of the epoxidation of allyl chloride with H_2O_2 over organic base treated TS-1 catalysts

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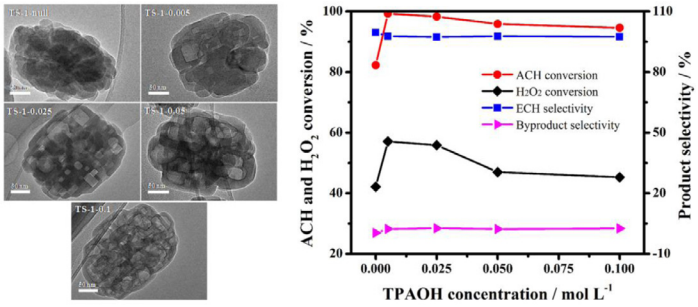
HIGHLIGHTS

- A large number of mesopores are formed in the TS-1 treated with TPAOH crystals.
- The systematic experimental study of allyl chloride epoxidation is reported.
- The modified TS-1 catalysts show better catalytic activity than TS-1 catalyst.
- Reaction kinetics of allyl chloride epoxidation over modified TS-1 is studied.

GRAPHICAL ABSTRACT



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ABSTRACT

An efficacious approach to improve the catalytic performance of titanium silicalite-1 (TS-1) catalysts in epoxidation of allyl chloride with hydrogen peroxide has been developed. A series of modified TS-1 catalysts were prepared by corroding the classic TS-1 catalyst with different concentrations of tetrapropyl ammonium hydroxide (TPAOH) under controlled conditions. The resultant catalyst samples were characterized by XRD, ICP, N_2-adsorption, FT-IR, UV–vis, SEM and TEM. The catalytic activity of the modified TS-1 catalysts is significantly improved, which could be attributed to the increase of the mesopore volume and pore diameter and decrease of the diffusion limitation but without obvious changes of the framework structure, framework Ti content, the outer surface shape and crystal size of the modified TS-1. Furthermore, the kinetics of the epoxidation of allyl chloride over TS-1-0.05 catalyst was also systematically studied, the apparent orders of reaction with respect to H_2O_2 and allyl chloride are 0.68 and 0.62, respectively, and the activation energy of the epoxidation reaction on the TS-1-0.05 catalyst is 57.4 kJ mol^{-1}.

1. Introduction

Epichlorohydrin (ECH) is an important chemical intermediate mainly used in the production of epoxy resins, chlorohydrin rubber, glycerin, etc [1–6]. In the present industrial processes, the traditional production methods of manufacturing ECH are the chlorohydrin method and the allyl alcohol method. As far as we

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Nomenclature

C_i	concentration of species i (mol L^{-1})	S_i	selectivity to product i (%)
n_i^0	initial number of moles of species i (mol)	r_0	initial reaction rate (mol L^{-1} min^{-1} g^{-1} cat)
n_i	number of moles of species i (mol)	Ea	apparent activation energy of the reaction (kJ mol^{-1})
X_i	conversion of species i (%)		

know, both methods have some obvious defects, the former process produces a large quantity of calcium chloride ($CaCl_2$) byproduct and halogen-containing wastewater, which is a serious problem with environmental pollution, and the latter process is very complicated and more costly manufacture. However, more than 90% of ECH in the world is still manufactured today using the chlorohydrin method [1,7–9]. Therefore, developing greener techniques for ECH production still remains a challenge and needs to be further explored. Titanium silicalite-1 (TS-1) with an MFI structure was first synthesized by Taramasso in 1983 [10], which is a selective catalyst oxidizing substantial amounts of organic compounds, such as olefins, alkanes, phenols and alcohols, with hydrogen peroxide (H_2O_2) under the mild reaction conditions [11–15]. As a green catalysis material, TS-1 has been applied to the ECH production from the epoxidation of allyl chloride (ACH) with H_2O_2 using methanol as a solvent [4,8,16–18]. The detailed reactions are shown in Scheme 1.

The TS-1 is a typical microporous catalyst with the average pore size of 0.55 nm, and its catalytic performance is strongly affected by the molecular size of substrate, nature of solvent, crystal size and pore structure [19]. However, the bulky products molecular may block the micropores of TS-1, which will display a negative effect on the diffusion of substrates. Therefore, eliminating the diffusion limitation is the key point of the catalytic performance of TS-1 in the catalytic oxidation reaction. In order to develop the high performance catalyst, researchers have tried to improve the catalytic activity and stability of TS-1 by various methods. Many modified TS-1 catalysts are prepared and reported, such as carbon template mesoporous TS-1 [20], SiO_2 pellet supported TS-1 film [17], Ti-rich TS-1 [21], clay minerals supported TS-1 [22], and organic bases modified TS-1 [23,24]. By treating the classic/commercial TS-1 with dilute organic base, the TS-1 catalyst can be modified with hierarchical structure and micro/mesoporous composite, which means it can be used as an efficacious method to improve the diffusion property, decrease the diffusion limitation, and enhance the catalytic performance of TS-1.

Herein, in order to enhance the catalytic activity of TS-1 in the epoxidation of allyl chloride process, we report on the synthesis and characterization of a series of new modified TS-1 catalysts, which were prepared by corroding the classic TS-1 catalyst with different concentrations of tetrapropyl ammonium hydroxide (TPAOH) under controlled conditions. Moreover, the corresponding catalytic performance of these new modified TS-1 catalysts were systematically investigated, including the effects of TPAOH concentration, catalyst content, allyl chloride:H_2O_2 (molar ratio), reaction time and temperature on the allyl chloride epoxidation. To have a good understanding of this reaction system, kinetics of the epoxidation of allyl chloride over TS-1-0.05 catalyst was systematically developed.

2. Experimental

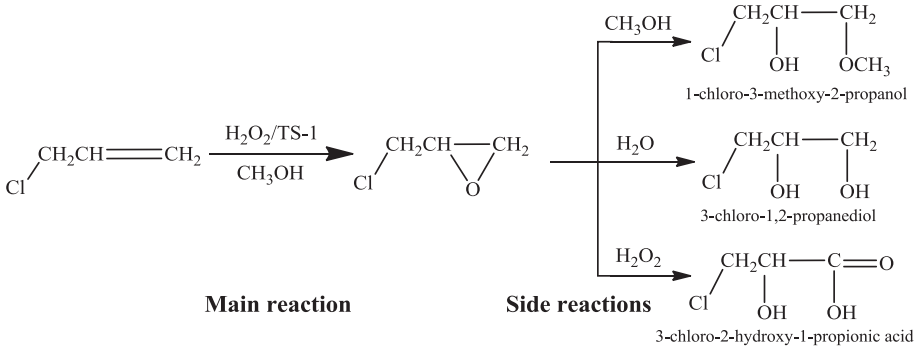
2.1. Materials

Tetraethyl orthosilicate (TEOS) and allyl chloride were purchased from Aladdin Chemistry Co. Ltd., China. Tetrabutyl titanate (TBOT), isopropyl alcohol, methanol, and 30 wt.% hydrogen peroxide were purchased from Tianjin Guang Fu Fine Chemical Research Institute Co., Ltd., China. 25 wt.% TPAOH was purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Synthesis of catalyst samples

TS-1 was synthesized according to literatures with modification [25,26]. In brief, a solution of 1.29 g TBOT, 7.9 g dried isopropanol and 31.5 g TEOS were dropwisely added into a 49.8 g solution of 15% TPAOH in water over 40 min with vigorous stirring under N_2 atmosphere. The composition of the final solution was SiO_2:0.025-TiO_2:0.24TPAOH:26.30H_2O (molar ratio). After further stirring for 2 h, the mixture was heated to 353 K and kept at this temperature for 1.5 h to remove alcohol. During this time, deionized water was added to compensate for the weight loss. Then the mixture was transferred into a 100 mL PTFE lined stainless steel autoclave and crystallized at 448 K for 72 h under static conditions. After cooling to the room temperature, the crystalline product was obtained by filtration, washed with deionized water to pH = 7, dried for 6 h at 393 K, and finally calcined for 5 h at 823 K in air. And this unmodified TS-1 sample was denoted as TS-1-Null.

The parent TS-1 was treated with TPAOH solution of x mol L^{-1} (TS-1-x) hydrothermally at 443 K for 24 h, with x varied at 0.005, 0.025, 0.05 and 0.1, respectively. The mass ratio of liquid/TS-1 was 10. The TPAOH treated TS-1 sample was separated by centrifu-



Scheme 1. Reaction pathways in the epoxidation of allyl chloride [17].