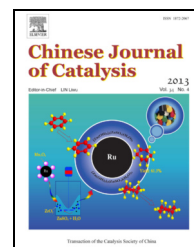


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Article

Effect of metals on titanium silicalite TS-1 for butadiene epoxidation

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ARTICLE INFO

Article history:

Received 29 October 2012

Accepted 21 November 2012

Published 20 April 2013

Keywords:

Butadiene

Epoxidation

Vinylloxirane

Metal

Titanium silicalite-1

ABSTRACT

The titanium silicalite-1 (TS-1) modified by various metals (M-TS-1; M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, La, 1% metals loading) catalysts were employed to catalyze butadiene epoxidation. The metals influenced the TS-1 activity in various ways. V, Cr, and Mn caused H₂O₂ decomposition. Although the H₂O₂ conversion was high, its utilization was relatively low. The introduction of Fe, Co, Ni, and La into TS-1 promoted the vinylloxirane (VO) yield and H₂O₂ utilization to some extent. Cu and Zn modification inhibited the H₂O₂ conversion to VO, resulting in both low H₂O₂ utilization and conversion. We studied the influence of Cd on TS-1 and found that H₂O₂ was almost totally converted to VO over the Cd-TS-1 catalyst, and the turnover number of VO reached 1197. Powder X-ray diffraction, N₂ adsorption and desorption, X-ray photoelectron spectroscopy, and Fourier transformed infrared spectra were employed to characterize the specific metal role at the Ti site in the M-TS-1 catalysts. The TS-1 remained as MFI structure with doped metals. The added metals effectively changed the electron environment of the Ti active site. However, no universal trend in behavior was observed for these metals.

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1. Introduction

Epoxidation of alkenes, especially low olefins is of great interest. Ag/Al₂O₃ catalysts [1–6], transition metal oxide nanoparticles (TiO₂, MnO₂, NiO, CoO, etc.) and their modifying catalysts [7–11], along with all kinds of titanium silicalite materials such as TS-1, TS-2, Ti-β, Ti-MCM-41/48, and Ti-MWW [12–16] have been applied as catalysts for alkene epoxidation. TS-1 exhibits outstanding properties of shape selective catalysis oxidation for low olefin epoxidation (propylene [17], butadiene [18]), owing to its unique structure and highly activated tetrahedral Ti centers inside the skeleton. Epoxidation reactions over TS-1, which can be performed under mild reaction conditions (0–100 °C, low pressure) with high activity and selectivity, are environmentally benign. In the epoxidation of low ole-

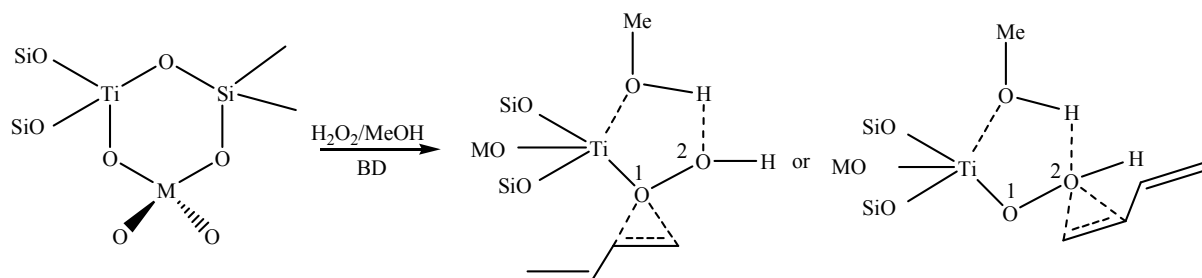
fins, O₂, H₂/O₂, H₂O₂, and *tert*-butyl hydroperoxide are usually used as oxidants. The activated oxygen content of H₂O₂ reaches up to 47% and H₂O₂ is environmentally benign as it forms H₂O as the only by-product [19]. Therefore, H₂O₂ is considered as the best choice of oxidant in the TS-1 catalytic system. Methanol is usually employed as the solvent in alkene epoxidation. A five-membered-ring intermediate (Clerici-like cycle), in which the double bond of the olefin bonds well with the activated oxygen in the H₂O₂, can be formed from the tetrahedral Ti in TS-1, H₂O₂, and methanol. Generally, TS-1/H₂O₂/methanol provides an effective catalytic system for low olefin epoxidation.

Transition metals, whose unoccupied 3*d* orbitals are good electron acceptors, display superior catalytic performance in redox reactions. They have been exploited extensively to mod-

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This work was supported by the National Natural Science Foundation of China (21133011).

DOI: 10.1016/S1872-2067(11)60498-1 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 34, No. 4, April 2013



Scheme 1. Five-membered-ring intermediate of butadiene epoxidation catalyzed by M-TS-1.

ify TS-1 in recent years. For example, the activity of TS-1 had been improved effectively with Zn [20], Ni [21], Co [22], and V [23] modification. In our early studies [21], TS-1 zeolite modified with metal Ni effectively catalyzed butadiene epoxidation. The interaction between Ni and TS-1 changed the electronic environment of the Ti centers. The peripheral electronic cloud around the Ti center was attracted by an embedded Ni 3d orbital and the electrophilicity of the Ti center and active oxygen were enhanced. This activated the double bond epoxidation of butadiene (as shown in Scheme 1). In addition, rare earth metals commonly considered as electronic auxiliaries are widely used in the catalytic field.

In recent years, although the significance of metal modification has been of great interest, further studies on the modification effect of metals (transition or rare earth metals) on TS-1 need to be conducted systematically. Meanwhile, vinyloxirane (VO) shows great value as an intermediate in synthesizing organic chemistry and chemical technology [19,24,25], and butadiene epoxidation is an attractive route to produce VO. Therefore, typical transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) and one rare earth metal (La) were exploited to modify TS-1 in this work. Butadiene (BD) epoxidation was used as a probe reaction, so as to explore the effect of metals on TS-1 catalytic performance.

2. Experimental

2.1. Catalyst preparation

The AR grade chemicals, NH_4VO_3 , $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and methanol (CH_3OH) were supplied by a local vendor. All chemicals were used without further purification. Concentrations of H_2O_2 (50%; local vendor) were determined by iodometric titration prior to use. Titanium silicalite 1 (TS-1, $\text{SiO}_2/\text{TiO}_2 = 40$) with specific surface area $463.1 \text{ m}^2/\text{g}$ was from Shanghai Novel Chemical Technology Co. Ltd.

The typical synthesis process was as follows: 1.00 g of TS-1 was dissolved in 5 ml distilled water, and the required amount of metal nitrate solution was added into the resultant solution with vigorous stirring. The mixture was treated under ultrasound, placed into an infrared drying oven with vigorous stirring until it changed to dry powder and finally dried overnight at $120 \text{ }^\circ\text{C}$. The final powder was calcined at $550 \text{ }^\circ\text{C}$ for 6 h.

2.2. Physicochemical characterization

Powder X-ray diffraction (XRD) measurements were performed using an X'Pert Pro multipurpose diffractometer (PANalytical, Inc.) with Ni-filtered $\text{Cu K}\alpha$ radiation (0.15046 nm) from 10.0° to 80.0° . Measurements were conducted using a voltage of 40 kV, current setting of 40 mA, step size of 0.02° , and count time of 4 s.

The N_2 adsorption and desorption isotherms at $-196 \text{ }^\circ\text{C}$ were recorded on an Autosorb-iQ analyzer (Quantachrome Instruments, U.S.). Prior to the tests, samples were degassed at $200 \text{ }^\circ\text{C}$ for 4 h. The specific surface areas were calculated via the BET method in the relative pressure range of 0.05–0.30; pore size distributions were calculated using adsorption branches of nitrogen adsorption-desorption isotherms by Saito-Foley (SF) methods.

The oxidation state of titanium and metals was characterized over a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectroscope (XPS). The M-TS-1 powder was pressed to form a self-supporting wafer prior to analysis.

Fourier transformed infrared (FT-IR) spectra of the M-TS-1 samples were recorded on an FT-IR spectrometer (Nicolet Nexus 870) with a resolution of 4 cm^{-1} and 64 scans in the region of $4000\text{--}400 \text{ cm}^{-1}$.

2.3. Catalytic reactions

The epoxidation of butadiene was performed in a 100 ml stainless-steel autoclave with magnetic stirrer. Typically, 0.40 g M-TS-1 and the designated amount of H_2O_2 were dispersed in 25.00 ml methanol solvent, and the autoclave was then sealed. Butadiene at 0.15 MPa was introduced into the autoclave through a needle valve. The slurry was heated to $40 \text{ }^\circ\text{C}$ with vigorous stirring, maintained at $40 \text{ }^\circ\text{C}$ for 60 min, and then quickly quenched in an ice water bath to around $0 \text{ }^\circ\text{C}$. The remaining H_2O_2 concentration was determined by standard iodometric titration. The liquid products that were formed were confirmed by gas chromatography-mass spectroscopy (GC-MS 5973, Agilent Technology Company). VO was confirmed as the main product, and the main by-products were small amounts of tetrahydro-2-furanmethanol and 4-ethenyl-cyclohexene. The quantity of products was determined using a gas chromatograph (SP-6800A GC) equipped with flame ionization detector and OV-1701 capillary column. The VO yield was determined

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