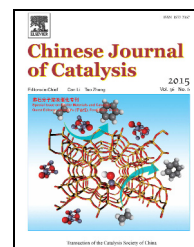


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Heterogeneous oxidation of cyclohexanone catalyzed by TS-1: Combined experimental and DFT studies



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ABSTRACT

The reaction mechanism of the oxidation of cyclohexanone catalyzed by titanium silicate zeolite TS-1 using aqueous H₂O₂ as the oxidant was investigated by combining density function theory (DFT) calculations with experimental studies. DFT calculations showed that H₂O₂ was adsorbed and activated at the tetrahedral Ti sites. By taking into account the adsorption energy, molecular size, steric hindrance and structural information, a reaction mechanism of Baeyer-Villiger oxidation catalyzed by TS-1 that involves the activation of H₂O₂ was proposed. Experimental studies showed that the major products of cyclohexanone oxidation by H₂O₂ catalyzed by a hollow TS-1 zeolite were ϵ -caprolactone, 6-hydroxyhexanoic acid, and adipic acid. These products were analyzed by GC-MS and were in good agreement with the proposed mechanism. Our studies showed that the reaction mechanism on TS-1 zeolite was different from that on Sn-beta zeolite.

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1. Introduction

Baeyer-Villiger (BV) oxidation is an important organic reaction by which esters or lactones are produced from ketones. Esters and lactones are important organic intermediates in chemical processes [1–6]. For example, ϵ -caprolactone, which is widely used to synthesize polymers, is produced from cyclohexanone. Traditionally, peracids, e.g. perbenzoic acid, *m*-chloroperbenzoic acid and trifluoroperacetic acid, are used as oxidizing agents in BV oxidation reactions [7–12]. Although the use of a peracid can lead to very high ketone conversion and fast product transformation, it is desirable to find cheaper and less polluting routes for BV oxidation for the preparation of

lactones on the commercial scale [13–19].

Aqueous H₂O₂ solution (usually 30 wt%–50 wt%), which is environmentally-friendly, cheap and easy to handle, has been introduced as the oxidant to replace hazardous peracids. One drawback is that H₂O₂ is less effective than peracids in attacking nucleophiles in order to activate the carbonyl group of ketones. In previous works, much effort was devoted to develop both homogeneous and heterogeneous catalysts in order to improve the performance of BV oxidation of cyclohexanone [20–24].

Heterogeneous catalysts have an important advantage over homogeneous ones for industrial applications because it is easier to separate the catalyst from the reactants and products

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[25–28]. There are two possible strategies to accelerate the heterogeneous BV oxidation of cyclohexanone using aqueous H_2O_2 solution (especially 30 wt%): (1) activate the carbonyl group of cyclohexanone with a Lewis acid catalyst to make the carbonyl C atom more easily attacked by the H_2O_2 molecule [29–32]; (2) increase the nucleophilicity of H_2O_2 molecules by forming more nucleophilic M-OOH species (M represents transition metal ions, which can accept the lone electron pairs of O atoms in the H_2O_2 molecules by employing their empty 3d orbitals) [33–38]. One excellent example is the Sn-beta zeolite catalyzed BV oxidation of cyclohexanone reported by Corma and coworkers, in which the lactone selectivity was close to 100% [22]. The Sn-beta zeolite has unique Lewis acid properties that make the carbonyl group more reactive to be attacked by H_2O_2 molecules. The Lewis acid site, especially in the form of $\text{Sn}(\text{SiO})_3\text{OH}$, can accept the lone electron pair from the cyclohexanone molecule, causing the electron cloud of the O atom in the carbonyl group to move towards the tetrahedral Sn atoms. As a consequence, the C atom in the carbonyl group becomes more easily attacked by H_2O_2 molecules.

In addition, it is well known that Ti-containing zeolites (in particular TS-1 zeolite) are good candidates to enhance nucleophilic attack by H_2O_2 molecules under moderate conditions, since the Ti atoms can accept the lone electron pairs of H_2O_2 by using its empty 3d orbitals to form a Ti-OOH species [39–42]. The Ti-OOH species is much more reactive than H_2O_2 , so nucleophilic attack of the C atom of the carbonyl group in cyclohexanone can be enhanced. Previous reports on BV oxidation of cyclohexanone catalyzed by TS-1 zeolite showed that many different products were formed in the absence of an organic solvent because ϵ -caprolactone was not stable and the Ti-OOH species could promote both the main BV oxidation and the side reactions simultaneously. Therefore, side products were obtained by consecutive ring opening and deep oxidation reactions.

There is no theoretical study of the mechanism of BV oxidation catalyzed by TS-1 zeolites using H_2O_2 as the oxidant. Here, we present a mechanistic study of the heterogeneous oxidation of cyclohexanone catalyzed by TS-1 zeolite using H_2O_2 as the oxidant based on density functional theory (DFT). We also performed catalytic experiments using a hollow TS-1 (HTS-1) zeolite [43–45] as the catalyst for the heterogeneous oxidation of cyclohexanone, and showed that the results support the proposed reaction mechanism.

2. Experimental

2.1. Synthesis of HTS-1 zeolite and catalytic experiments of the heterogeneous oxidation of cyclohexanone

First, TS-1 zeolite was prepared according to a conventional method [41]. Tetraethyl orthosilicate and titanium butoxide were added dropwise to an aqueous tetrapropylammonium hydroxide (TPAOH) solution under continuous stirring. The molar ratio of $\text{TiO}_2:\text{SiO}_2:\text{TPAOH}:\text{H}_2\text{O}$ was 0.03:1.00:0.15:22.0. The mixture was heated at 80 °C for 4 h to remove the alcohols, then transferred into a Teflon-lined stainless steel autoclave,

and heated at 170 °C for 72 h under autogeneous pressure. The product, TS-1 zeolite, was collected by filtration, washed with water, and calcined at 550 °C in air for 6 h.

HTS-1 zeolite was synthesized from calcined TS-1 zeolite in an aqueous TPAOH solution at 170 °C for 24 h according to the literature [43,45]. X-ray powder diffraction (XRD) results showed well-crystallized TS-1 and HTS-1 powders with the MFI structure (Fig. S1). Transmission electron microscopy (TEM) images showed uniformly sized TS-1 and HTS-1 particles with mesopores present in the HTS-1 particles (Fig. S2). N_2 adsorption isotherms showed that HTS-1 contained mesopores (Fig. S3). The BET surface areas and pore volumes of TS-1 and HTS-1 are given in Table S1.

The heterogeneous oxidation reaction of cyclohexanone using H_2O_2 as the oxidant was carried out in a 100-ml three-necked flask under magnetic stirring. A mixture of the HTS-1 zeolite catalyst (5 wt%) and 0.01 mol cyclohexanone, either without an organic solvent or in the presence of an organic solvent (acetone or methanol), was added into the flask and heated to the reaction temperature. Then H_2O_2 solution (0.01 mol, 30 wt%) was injected into the flask. After several hours (4 or 8 h), a small amount of the mixture was extracted from the flask and analyzed by an Agilent 6890 gas chromatograph with a 3-m HP-5 column and hydrogen flame ionization detector. The main products and side products were confirmed by gas chromatography-mass spectrometry (GC-MS) on an Agilent 5977A series GC/MSD system.

2.2. Molecular models and computational methods

TS-1 has the MFI zeolite topology with the unit cell parameters $a = 20.13 \text{ \AA}$, $b = 19.95 \text{ \AA}$, $c = 13.42 \text{ \AA}$ [1]. There are 12 symmetry-independent and a total of 96 T-atoms in a unit cell. It has a three dimensional 10-ring channel system with straight channels along the [010] direction and sinusoidal channels perpendicular to the straight channels. The highest Ti content in the TS-1 framework was 2.5 mol% ($\text{Si}/\text{Ti} = 39$), i.e., on average two Si atoms in each unit cell were substituted by Ti atoms. To understand the adsorption and activation of cyclohexanone and H_2O_2 at the active sites of TS-1 zeolite, a $\text{Ti}(\text{OSiH}_3)_4$ cluster model was used [1–3], as shown in Fig. 1. The cluster was cut from the TS-1 zeolite structure and contains one Ti atom at the T7 site connected to four $-\text{O}-\text{SiH}_3$ fragments. The direction of each H atom in the cluster was set to be the same as that of the corresponding O atom in the TS-1 zeolite framework in order to use the actual structure for the active site. The adsorption and activation of cyclohexanone and H_2O_2 on the active Ti site were calculated by the Adsorption Locator module in the MS software. The transition states were analyzed by using the effective core potential method and the DMol3 module in the MS software which uses the LST/QST protocol and employs the GGA/PW91 technique. Furthermore, the $\text{Ti}(\text{OSiH}_3)_3\text{OH}$ cluster was considered as the active site for BV catalytic oxidation in TS-1 zeolite [39]. Its geometry optimization of the reaction pathway was performed using the B3PW91 method in order to investigate the mechanism of the catalytic oxidation of cyclohexanone.

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