



Cyclohexane mild oxidation catalyzed by new titanasilicate with hollow structure

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ABSTRACT

Titanium silicalite with hollow structure (HTS), was one new type of titanasilicate used in oxidation process. Its catalytic property on the mild oxidation of cyclohexane with hydrogen peroxide (H_2O_2) in liquid phase was investigated, and the difference of catalytic performance between HTS and compared sample (TS-1) was discussed. The results show cyclohexanone (K) and cyclohexanol (A) are the major products; with the increment of reaction temperature and reaction time, cyclohexane conversion and the yield of K increase, the selectivity to K increases while the selectivity to A decreases. It is found that hollow structure and different distributions of Ti species lead to above differences, and L acidity would be also concerned with their catalytic performance. In one word, HTS is one proper catalyst for application in the cyclohexane oxidation process with H_2O_2 as oxidant under mild conditions.

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1. Introduction

Cyclohexanone (K) and cyclohexanol (A) (the mixture is known as K–A oil) are important chemicals and raw materials because they are the key precursors for the production of caprolactam and adipic acid, which in turn are important intermediates in the manufacture of nylon-6 and nylon-66, respectively (Scheme 1) [1,2]. K–A oil are mainly obtained by the oxidation of cyclohexane with air [3,4], current industrial process uses a soluble cobalt carboxylate or metal–boric acid catalyst to produce a mixture of cyclohexanone, cyclohexanol and other products with ~80% selectivity to K–A oil. The air oxidation reaction is usually carried out at ~443 K and ~11 bar of atmospheric pressure, cyclohexane conversion is limited to less than 10% to reduce over oxidation to unwanted products, since the primary products (cyclohexanone and cyclohexanol) are more reactive than the reactant (cyclohexane) [5]. Apart from low conversion (<10%) and extreme reaction conditions, this process produces several by-products, such as mono- and/or di-carboxylic acids, esters, and other oxygenated materials [6]. In addition, the industrial process produces more amount of cyclohexanol, and additional steps are needed to improve the cyclohexanone/cyclohexanol mole ratio (K/A) in the final products [7].

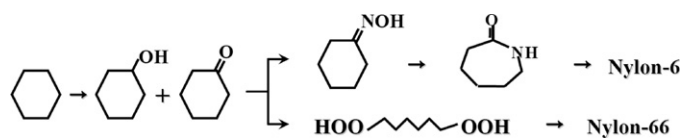
To overcome these defects, attempts have been made to prepare more efficient catalysts or to ameliorate the engineering technologies in cyclohexane oxidation. Moreover, the significant industrial demand in recent years (~10 million ton/year in 2006) of K–A oil has stimulated various studies aiming to find milder, lower-cost, and more environmentally friendly conditions, namely to find alternative greener and more effective catalytic processes for the classic industrial method [8,9], which means that the yield and selectivity to K–A oil should be enhanced in a less polluted process. From the point of view of oxidant, with respect to various of oxidants, hydrogen peroxide (H_2O_2 , HP) is a preferable one and as one versatile and green oxidant, because of its containing of a high fraction of active oxygen, simplicity of handling and environmentally benign nature of the co-product (water) in oxidation reaction [10], so the investigation of an efficient catalyst for the oxidation of alkanes especially for cyclohexane with HP as oxidant is very attractive.

Titanium silicalite (TS-1) is a molecular sieve with MFI topological structure, in which small numbers of tetrahedral Si atoms are substituted by Ti atoms in a purely siliceous framework. The discovery of TS-1 zeolite in 1980s [11], offers one new opportunity for the oxidation of cyclohexane with HP as oxidant. With relative high cyclohexane conversion rate and high selectivity to K–A oil under mild conditions in liquid phase, this process is regarded as an alternative environmentally friendly route to substitute for old ones [12]. In our earlier studies, one new titanasilicate with hollow structure was presented (branded by HTS, having large intra-particle voids), which was skillfully synthesized via a route named dissolution-recrystallization process, enhancing the

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Scheme 1. Simplified route to the production of Nylon-6 and Nylon-66.

dimensions of the intra-particle pores without unduly sacrificing the microporous ones, and thus can intensify the transport of reactants and products in and out of the crystal's channels [13,14]. Here, for the first time, HTS was applied as catalyst to catalyze cyclohexane oxidation with HP, the differences of catalytic performance between HTS and compared sample (normal TS-1) were also discussed extensively. The catalysts were characterized by various instruments, from which the positive role of intra-particle voids within HTS crystals was evaluated. Furthermore, the controlling parameters of this greener oxidation process, such as reaction temperature and reaction time were also investigated, and then their different catalytic performances were tentatively associated with the L acidity of catalysts.

2. Experimental

2.1. Synthesis of HTS and compared sample TS-1

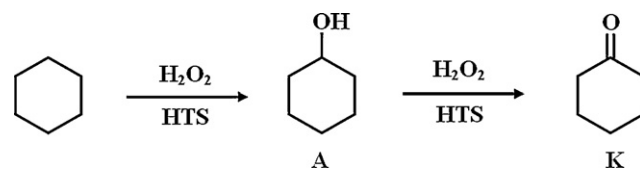
HTS and normal TS-1 (compared sample) were prepared using the procedures similar to that described in the literatures [13,14]. One typical preparation procedures of HTS and normal TS-1 were as follows: (1) 40 g tetraethyl orthosilicate (TEOS) was mixed with the solution containing 12 g tetrapropyl ammonium hydroxide (TPAOH) and 88 g distilled water thoroughly hydrolyzed at 65 °C for 2 h. To the resultant mixture, a solution composed of tetrabutyl orthotitanate (TBOT) and anhydrous isopropanol was added slowly with stirring. The mixture was further stirred at 65 °C for 1 h, then transferred to a stainless steel autoclave with Teflon-coated and shelved at 170 °C for 36 h. The product was recovered by filtration, washed with distilled water, air-dried at 100 °C for 4 h, and calcined in air at 500 °C for 4 h, normal TS-1 was obtained, (2) normal TS-1 was mixed with sulfuric acid solution and treated at room temperature for 5 h, with a weight ratio of normal TS-1:sulfuric acid:water = 10:1.0:150, and (3) the recovered acid-treated TS-1 was mixed with TPAOH solution in a weight ratio of molecular sieve:TPAOH:water = 10:1.5:120. Then, the mixture was treated at 140 °C for 72 h. After cooling and pressure unloading, routine recovery and calcination, HTS was obtained.

2.2. Characterization techniques

Rigaku 3271E X-ray fluorescence spectrometer was used to measure X-ray fluorescence analyses (XRF). Siemens D5005 diffractometer with nickel-filtered Cu K α radiation was used to record the powder X-ray diffraction data (XRD). Nicolet 8210 infrared spectrometer was used to record the data of infrared spectra (FT-IR). Perkin-Elmer Lambda 20 UV-visible spectrometer was applied to obtain the data of UV-visible spectra (UV-vis). Tecnai G²F20S-TWIN electron microscope was used to perform transmission electron microscopy (TEM) experiments. Philips XL 30 ESEM was used to collect scanning electron microscopy (SEM) images. Micromeritics ASAP 2010M system was used to measure nitrogen adsorption-desorption isotherms of samples.

2.3. Catalytic oxidation of cyclohexane to K-A oil

The experiments for cyclohexane oxidation reaction with HP as oxidant (Scheme 2) were carried out in a stainless-steel reactor



Scheme 2. Simplified reaction pathway of cyclohexane oxidation with H₂O₂ as oxidant catalyzed by HTS.

equipped with a Teflon beaker, electric stirrer and oil bath. Typically, 1.0 g catalyst, 2.1 g cyclohexane, 15 g acetone and 4.2 g HP (30 wt.% water solution), were charged to the reactor with stirring in one lot, the slurry was shelved and the reactor was kept at reaction temperature for different periods of time. The samples were periodically taken and then analyzed by Agilent 6890N GC equipped with a FID and a HP-5 capillary column (30 m).

3. Results and discussion

3.1. General characterization of HTS and TS-1

As determined by XRF analysis, HTS is composed of SiO₂ (97.28%) and TiO₂ (2.72%), and normal TS-1 contains SiO₂ (97.26%) and TiO₂ (2.74%) with the same level of Ti content. As examined by X-ray diffraction (Fig. 1), HTS exhibits almost the same main diffraction peaks as those in XRD of normal TS-1, and also accordant with those of the typical ZSM-5, indicating that both HTS and TS-1 are with MFI topological structure [15]. FT-IR spectra of HTS are also consistent well with those of TS-1, further indicating that HTS and TS-1 are with MFI topology and have intra-framework Ti [16,17]. In UV-vis spectra, both HTS and TS-1 give only one strong UV absorption bands at around 210 nm, not only indicating both HTS and TS-1 have intra-framework Ti species, but also demonstrating the Ti species in HTS and TS-1 are mainly existed as isolated tetrahedral

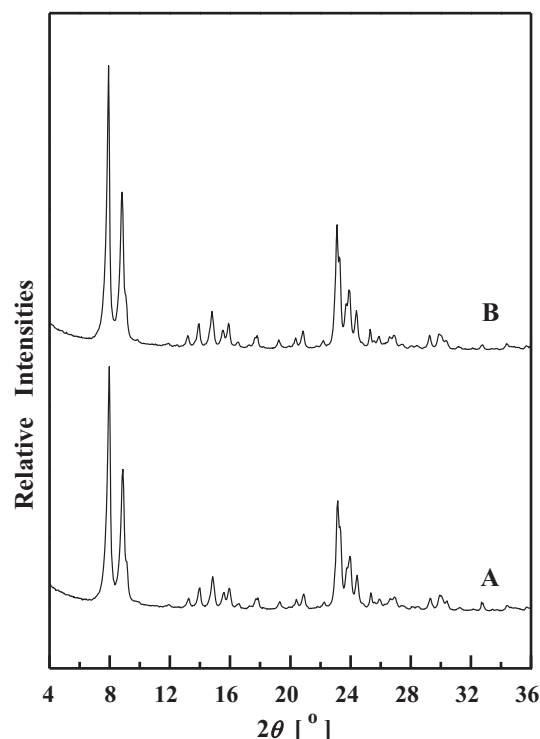


Fig. 1. The XRD patterns of samples: (A) HTS, and (B) TS-1.

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