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Catalytic oxidation of cyclic ethers to lactones over various titanosilicates

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ABSTRACT

Various crystalline microporous metallosilicates have been used in the liquid phase catalytic oxidation of different cyclic ethers into their corresponding lactones in the presence of dilute aqueous H_2O_2 as oxidant. Among the various metallosilicates studied for the oxidation of tetrahydrofuran to γ-butyrolactone, titanosilicates exhibited the best activity than the other metallosilicates such as chromium silicalite-1 (CrS-1), chromium silicalite-2 (CrS-2) and vanadium silicalite-1 (VS-1). The intrinsic activity of TS-1 was found to be marginally higher than the other titanosilicates. Cyclic ethers undergo α_{C-H} oxidation to give the corresponding lactones; whereas open-chain ether produce carboxylic acids by initial α_{C-H} bond oxidation to give ester as an intermediate product, which further undergoes cleavage of –O– linkage to give the final carboxylic acids. The conversion of substituted tetrahydrofuran is decreased with number of $-CH_3$ groups at α- and/or β-position. The lactone formation is hindered when both the α-positions are substituted with methyl substituents. Mechanistically, titanium hydroperoxo complex formed in the titanosilicate/H_2O_2/H_2O system is believed to oxidize the α_{C-H} bond of ethers producing the respective α-hydroxylated product, which undergoes further oxidation to give the lactones (for cyclic ethers) or carboxylic acids (for open-chain ethers).

1. Introduction

Selective oxidation is one of the key reactions in organic chemistry for the preparation of various intermediates and fine chemicals. However, most of these reactions catalyzed by homogeneous catalysts are stoichiometric and non-recyclable. Thus, in the fine chemical synthesis, there is a significant trend towards stoichiometric inorganic oxidants such as chromium and manganese compounds with a direct catalytic method using heterogeneous and environment-friendly catalysts, which are non-stoichiometric and recyclable. The discovery of TS-1 in 1983 [1] through isomorphous substitution of silicon by titanium in microporous MFI framework and its unique catalytic properties especially in selective oxidation reactions lead to industrial resurgence such as in the production of catechol and hydroquinone from phenol, cyclohexanone oxime from cyclohexanone using dilute aqueous H_2O_2 as oxidant. The advantage of high activity coupled with reusability, no byproduct formation and the ease of separation of the catalyst from reaction mixture, justified the use of TS-1 as the potential heterogeneous oxidation catalyst. In light of these developments, a variety of new titanium containing microporous crystalline materials such as Ti-ZSM-11 (TS-2) [2], Ti-ZSM-48 [3], Ti-β [4], Ti-MCM-22 [5], Ti-MWW [6] as well as mesoporous Ti-MCM-41 [7], Ti-HPVS-1 [8] and amorphous extra large pore Ti-DMS materials [9] have been successfully synthesized and studied for various oxidative transformations under liquid phase conditions. The advantage of transition metal containing microporous and mesoporous materials over homogeneous catalysts have already been successfully demonstrated for the epoxidation of alkenes, hydroxylation of phenol, ammoximation of ketones, and oxidation of alcohols, amines, sulfides, etc. using dilute H_2O_2 under eco-friendly liquid-phase conditions [10,11]. The oxidation of C–H bond in alkanes and benzene is an important area of research due to large scale industrial production of fine chemicals from cheaply available hydrocarbon feed stocks [12]. However, not much research has been carried out on the oxidation of C–H bond in cyclic as well as open-chain ethers using heterogeneous catalysts under liquid-phase conditions.

The selective oxidative functionalization at the α_{C-H} bonds of ethers is one of the most useful reactions in organic synthesis since it serves for efficient preparation of esters or lactones in the case of cyclic ethers [13]. Furthermore, the α-methylene-γ-butyrolactone structural unit is present in a wide variety of sesquiterpenes and other natural products, and has been suggested to be of central importance for the biological activities of those compounds [14]. These oxidation reactions are usually accomplished by the use of either stoichiometric amounts of chromium trioxide, lead tetraacetate, or ruthenium tetroxide as oxidant [15] or the catalytic amounts of RuO_4 in the presence of hypochlorite or periodate [16]

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Table 1
Physico-chemical properties of various titano- and metallo-silicates.

Entry	Catalysts	Si/M ratio[a]		Particle size[b]	Micropore volume ($mL\,g^{-1}$)
		Input gel	Final product		
1	TS-1	40	41.1	0.1–0.2 μm	0.14
2	TS-2	40	59.0	2–3 μm	0.12
3	Ti-β (OH)	40	43.0	0.2–0.3 μm	0.28
4[c]	Ti-β (F)	35.0	48.3	3–4 μm	0.22
5	Ti-MCM-22	45	51.0	0.2–0.5 μm	0.26
6	VS-1	60	96.0	0.4–0.6 μm	0.13
7	CrS-1	60	85.2	0.3–0.5 μm	0.12
8	CrS-2	60	72.1	1–2 μm	0.11

[a] Si/M ratio was estimated from ICP analysis.
[b] Particle size measurements were made from SEM analysis.
[c] Ti-β was synthesized under the fluoride medium.

under homogeneous conditions. Recently, several new oxidation systems have been described using transition metal complexes of Co, Pd, etc. as catalysts for the transformation of ethers to esters [17]. Although a number of different reagents have been discovered for the selective oxidation of ethers, only few have assumed any synthetic and/or industrial importance because of the expense of the catalysts, high acidity of the media, and poor selectivity in terms of product distribution. The use of heterogeneous catalysts in the liquid-phase, on the other hand, offers several advantages compared with their homogeneous counterparts [18]. In this context Sn-beta/H_2O_2 [19] and Sn-MCM-41/H_2O_2 [20] systems are successfully employed for the chemoselective Baeyer-Villiger oxidation of cyclohexanone to lactone. We have reported earlier, the facile catalytic oxidation of ethers with dilute H_2O_2 over TS-1 [21]. Herein, we report the detailed investigation of oxidation of cyclic ethers over various titanosilicates such as TS-1, TS-2, Ti-MCM-22, and Ti-β. The activity of these titanosilicates has been compared with other metallosilicates such as VS-1, CrS-1, and CrS-2 under similar experimental conditions. The activity and product selectivity has also been investigated with respect to substituent effect, substrate/H_2O_2 molar ratio and reaction time. The reusability of different titanosilicates after reactivation has also been investigated.

2. Experimental

2.1. Synthesis of TS-1, TS-2 and Ti-β

TS-1 was synthesized by modifying the standard literature procedure [22,23]. In a typical synthesis 54.2 g tetraethyl orthosilicate (98%, TCI) was hydrolyzed with 90 g of tetrapropylammonium hydroxide (20% aqueous, TCI) with vigorous stirring for 3 h. Then 2.12 g tetrabutyl orthotitanate (98%, Aldrich) dissolved in dry isopropanol was added drop wise to clear homogeneous solution and the stirring was continued for an extended period of time at 323 K in order to remove the ethanol formed from the hydrolysis of TEOS. Finally, 32 mL of water was added (gel composition: SiO_2:0.025 TiO_2:35 TPAOH:H_2O) and the mixture was allowed to crystallize in a rotating autoclave at 443 K for 24 h. After crystallization, the product was centrifuged and washed several times to remove the occluded organic template. Then the solid was dried and calcined at 773 K for 12 h in the presence of air. For the synthesis of the catalyst TS-2 TPAOH was replaced by tetrabutylammonium hydroxide (TBAOH, 40%, Aldrich). Synthesis gel was prepared keeping the gel composition: SiO:0.025 TiO_2:0.35 TBAOH:33.3 H_2O, followed by hydrothermal treatment under static condition at 443 K for 48 h [2].

The Ti-β was synthesized in a basic medium by modifying the reported procedure [4]. Titaniumperoxo complex was first prepared by the addition of $Ti(OBut)_4$ and H_2O_2 under vigorous stirring. This complex was then mixed with TEAOH (35% aqueous, Aldrich) followed by the addition of Aerosil-200 silica and 3% dealuminated seed crystals and the stirring was continued for an extended period to obtain a homogeneous gel. The resulting gel (chemical composition: SiO_2:0.025 TiO_2:0.337 H_2O_2:5 TEAOH:6.62 H_2O) was transferred into a Teflon-lined autoclave, and the crystallization was carried out at 413 K for 5 days. The as-synthesized materials were dried at 373 K and calcined in O_2 flow for 12 h at 793 K. The Ti-β(F) was synthesized by using HF (47% aqueous) as mineralizer in a gel composition of SiO_2:0.029 TiO_2:0.337 H_2O_2:0.55 TEAOH:0.55 HF:5.5 H_2O [10]. The gel was crystallized in a Teflon-lined autoclave at 413 K for 5 days. The as-synthesized materials were dried and calcined in O_2 slowly for 12 h at 793 K.

2.2. Synthesis of Ti-MCM-22

The Ti-MCM-22 was synthesized according to the reported procedure [5] from fumed silica (Cab-o-sil M7D), tetrabutyl orthotitanate ($Ti(Obut)_4$), boric acid, and piperidine (TCI, 98%). Piperidine was dissolved in deionized water and divided into two portions, and the required amount of $Ti(Obut)_4$ or boric acid was added to each piperidine solution under vigorous stirring. Further, silica was also divided into two equal parts and added to the solution containing Ti and B, respectively. The gels were stirred for 1 h and then mixed together. The combined gel was stirred for another 1.5 h to obtain a gel with a molar gel composition of SiO_2:0.02 TiO_2:0.67 B_2O_3:1.4 piperidine:19 H_2O. The crystallization of the resulting gel was carried out in a stirring autoclave at 403 and 423 K each for 1 day and further at 443 K for 5 days. After crystallization, the solid product was washed, dried, and the framework boron and extra-framework titanium were removed by acid treatment with 2 M HNO_3 at 373 K for 20 h. The samples were calcined at 803 K to burn off the remaining organic species.

2.3. Synthesis of other metallosilicates

The hydrothermal synthesis of CrS-1 [24] was carried out using the gel composition: SiO_2:0.017 Cr_2O_3:0.35 TPAOH:33.3 H_2O. In a typical synthesis, required amount of TEOS was added to an ice-cold solution of TPAOH and after complete hydrolysis $Cr(NO_3)_3{\cdot}9H_2O$ was added into the mixture. After evaporation of the ethanol produced through 4 h stirring at 323 K, the clear solution obtained was crystallized at 443 K under tumbling for 24 h. Similarly, CrS-2 was prepared using tetrabutylammonium hydroxide according to the reported procedures [25–28]. V-MFI was synthesized according to the procedure reported by Carati et al. [29]. $VOSO_4 \times H_2O$ (Aldrich, 99.9%) was used as the source of vanadium. In a typical synthesis, 21.0 g of TEOS in 20 mL of water was hydrolyzed with 41.0 g of tetrapropyl ammonium hydroxide (20% aqueous solution) for 3 h. Then, 0.45 of vanadyl sulfate was added, and the stirring was continued for another 3 h under the flow of helium gas in order to