



Catalytic oxidation of cyclic ethers to lactones over various titanasilicates

Manickam Sasidharan^a, Asim Bhaumik^{b,*}

^a Department of Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840-8502, Japan

^b Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

ARTICLE INFO

Article history:

Received 25 October 2010

Received in revised form 17 January 2011

Accepted 6 February 2011

Available online 12 February 2011

Keywords:

TS-1

Ether oxidation

Lactones

Tetrahydrofuran

Liquid phase oxidation catalysis

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 H₂O₂ as oxidant. Among the various metallosilicates studied for the oxidation of tetrahydrofuran to γ -butyrolactone, titanasilicates 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 titanasilicates. 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 titanasilicate/H₂O₂/H₂O 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).

© 2011 Elsevier B.V. All rights reserved.

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 H₂O₂ 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 H₂O₂ 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 RuO₄ in the presence of hypochlorite or periodate [16]

* Corresponding author.

E-mail address: msab@iacs.res.in (A. Bhaumik).

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/H₂O₂ [19] and Sn-MCM-41/H₂O₂ [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 H₂O₂ 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/H₂O₂ 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: SiO₂:0.025 TiO₂:35 TPAOH:H₂O) 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: SiO₂:0.025 TiO₂:0.35 TBAOH:33.3 H₂O, 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 H₂O₂ under vigorous stirring. This complex was then mixed with TBAOH (35% aqueous,

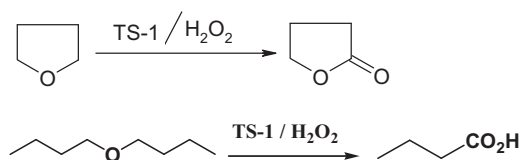
Aldrich) followed by the addition of Aerosil-200 silica and 3% dealuminated seed crystals and the stirring was continued for an extended period to obtain a homogeneous gel. The resulting gel (chemical composition: SiO₂:0.025 TiO₂:0.337 H₂O₂:5 TBAOH:6.62 H₂O) was transferred into a Teflon-lined autoclave, and the crystallization was carried out at 413 K for 5 days. The as-synthesized materials were dried at 373 K and calcined in O₂ 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 SiO₂:0.029 TiO₂:0.337 H₂O₂:0.55 TBAOH:0.55 HF:5.5 H₂O [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 O₂ 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 SiO₂:0.02 TiO₂:0.67 B₂O₃:1.4 piperidine:19 H₂O. 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 HNO₃ 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: SiO₂:0.017 Cr₂O₃:0.35 TPAOH:33.3 H₂O. In a typical synthesis, required amount of TEOS was added to an ice-cold solution of TPAOH and after complete hydrolysis Cr(NO₃)₃·9H₂O 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]. VOSO₄ × H₂O (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



Scheme 1. Catalytic oxidation of cyclic and open chain ethers over titanasilicates.

suppress the oxidation of V⁴⁺ to V⁵⁺ at high pH. Finally, 30 mL of water added and the clear homogeneous solution was subjected to crystallization at 443 K for 48 h. The white solid was washed with distilled water, dried at 373 K, and calcined at 773 K under the flow of O₂ through slow increase of the oven temperature. All the metallosilicates were thoroughly characterized through XRD, FT-IR, UV-Vis, SEM, sorption and surface area measurements and the composition by ICP analysis. Table 1 shows the important physico-chemical properties of different metallosilicates investigated under present study.

2.4. General liquid phase catalytic oxidations

The liquid-phase catalytic reaction was performed in a two-necked glass reactor fitted with a water condenser at 343 K under vigorous stirring. A typical reaction involves 10 mmol of substrate, 10 mmol of H₂O₂, and catalyst TS-1 (Si/Ti = 41), 20 wt% with respect to the substrate. The reaction was carried out in the absence of any cosolvents. Cycloheptanone was used as internal standard for quantification of products. The progress of the reaction was monitored by analyzing the products obtained at different intervals through a capillary gas chromatograph (Shimadzu 14A, OV-1 columns with flame ionization detectors). The products were identified by GC-MS splitting pattern as well as from authentic samples and in some cases the mixture is distilled off to obtain pure products and analyzed through GC-MS and ¹H NMR.

3. Results and discussion

3.1. Activity of various titano- and metallosilicates

Table 2 shows the activity of various metallosilicates in the oxidation of tetrahydrofuran to gamma-butyrolactone (Scheme 1). The medium-pore TS-1 exhibits (entry 1) comparatively higher activity over the large-pore Ti-beta. TS-2 and Ti-MCM-22 (entries 2 and 3) show moderately lower activities than that of TS-1. This could be attributed to the higher Si/Ti ratio coupled with larger crystal-size of the respective catalysts rather than diffusion limitation, which is almost negligible for molecule with small dimension such as tetrahydrofuran. Although both TS-1 (Si/Ti = 41.1) and Ti-beta(OH) (Si/Ti = 43) have similar titanium content and crystal sizes of 0.1–0.2 μm and 0.2–0.3 μm, respectively, the former exhibits more activity than the later (entry 4). On first glance it was assumed that, unlike TS-1, the structure of Ti-beta itself slightly hydrophilic in nature even in the complete absence of aluminum, which leads to competitive adsorption of both reactant as well as H₂O inside the pores and channels, and eventually decreased the activity of Ti-beta. However, Ti-beta(F) synthesized in the fluoride medium (entry 5), supposed to be the better hydrophobic catalyst, realized still lower activity (40.3%) presumably due to its lower titanium content coupled with larger particle-size. Moreover, Ti-beta(OH) exhibited higher TON than the Ti-beta(F) and therefore, the hydrophobicity cannot be the major determining factor of the activity between TS-1 and Ti-beta(OH). Nonetheless, the turn over frequencies of different titanosilicate changes within a range (4.3–5.2) and the intrinsic activity of TS-1 are comparatively higher than the other titanosilicates investigated. Loading of chromium in silicalite-1 and silicalite-2 (entries

6 and 7) exhibit poor activity for the oxidation of C–H bond in tetrahydrofuran, even though it showed better activity for other functional groups oxidation [30–32]. Similarly, VS-1 also realized lower activity under identical conditions (entry 8).

In order to compare the lactone selectivity at similar conversion levels as that of Cr- and V-silicates, additional experiments were performed by reducing the reaction time over the titanosilicates; thus TS-1, TS-2, Ti-MCM-22, and Ti-beta exhibited 85.7, 83.8, 86.0 and 88% selectivities at the conversion of 10.5, 8.3, 7.2, and 9.0%, respectively. The above results suggest that selectivity for gamma-butyrolactone is almost similar for titanium and chromium silicates; whereas VS-1 gives slightly more side-products. In the case of Cr- and V-silicates, in order to obtain information on the low reactivity as well as to find out leaching of metal atoms, the catalyst was filtered off, organics were removed through evaporation, and the residual solution was analyzed by using an AAS. Leaching of chromium was found to be 28 and 36% for CrS-1 and CrS-2, respectively; whereas that for vanadium in VS-1 showed 33% on extraction. However, neither vanadium nor chromium exhibited the oxidation of tetrahydrofuran under homogeneous conditions. In addition, there is not much difference in selectivity of lactone at similar conversion levels of tetrahydrofuran for different titanosilicates: In view of these above observations titanosilicates have been chosen for further investigations.

3.2. Oxidation of various cyclic- and open-chain ethers over TS-1 and Ti-beta

The results of the oxidation of various cyclic and open-chain ethers over both TS-1/H₂O₂ and Ti-beta/H₂O₂ catalytic systems are presented in Table 3. Entries 1–4 demonstrate the oxidation of tetrahydrofuran and substituted tetrahydrofurans to the corresponding lactones. The intrinsic activity of TS-1 is slightly higher than that of Ti-beta (entry 1) for simple unsubstituted tetrahydrofuran. However, the activity of TS-1 is influenced by the bulkiness of tetrahydrofuran derivatives and it decreased drastically when a methyl group is located on one of the alpha-positions (entry 2). The marginal difference in reactivity between TS-1 and Ti-beta indicates that, the effect of methyl substituent at the alpha-position is comparatively more pronounced for the former due to geometrical constraints to approach to the metalperoxide or reaction sites. Furthermore, the presence of two methyl groups at alpha, alpha'-position of tetrahydrofuran (entry 3) not only leads to lower reactivity but also reduced the selectivity presumably due to steric hindrance as well as difficulty associated with the cleavage of C–C bond to produce the corresponding lactone. Thus the observed results over the titanosilicates are unique in the sense that the reactivity of the C–H bond at tertiary carbon is supposed to be higher than the secondary and/or primary one for homogeneously catalyzed reactions [11]. Therefore, the decreased reactivity of alpha-methyl substituted tetrahydrofuran may be due to the inductive effect and steric hindrance of these molecules exerted at the active-sites located in the porous framework. The oxidation of tetrahydrofuran is negligible for both TS-1 and Ti-beta when all available alpha-positions are substituted with methyl groups (entry 4) and it is obvious that the lack of alpha-C–H bond results in no lactone formation.

Entry 5 shows the oxidation of tetrahydropyran to delta-valerolactone, and again TS-1 is slightly more active than Ti-beta as observed in the case of unsubstituted tetrahydrofuran. For substituted tetrahydropyrans, the presence of methyl group at the beta-position (entry 6) also decreases the reactivity. The oxidation of dihydropyran (entry 7) leads to a mixture of delta-valerolactone and epoxy products through epoxidation of C=C– double bond. Thus in the presence of C=C– double bond, the alpha-C–H of ethers seems to be less reactive and subsequently leads to decreased lactone selectivity. Therefore, the conversion of ethers to lactones lacks functional

Table 2
Activity of various metallosilicates in the oxidation of tetrahydrofuran.^a

Entry	Catalyst	Conv. (mol%)	H ₂ O ₂ sel.%	TOF ^b	Product selectivities, %		
					γ-Butyrolactone	α-Hydroxy tetrahydrofuran	Others ^c
1	TS-1	49.0	99.0	5.2	91.0	3.6	5.4
2	TS-2	32.3	87.0	4.3	90.1	4.0	5.9
3	Ti-MCM-22	37.5	93.0	4.5	89.0	4.8	6.2
4	Ti-β(OH)	45.2	97.0	4.7	90.4	4.9	4.7
5 ^d	Ti-β(F)	40.3	85.9	4.6	91.3	4.8	3.9
6	CrS-1	8.0	68.0	1.8	89.0	2.8	8.1
7	CrS-2	6.9	62.0	1.3	87.3	3.9	8.8
8	VS-1	7.1	7.0	1.6	78.0	4.9	17.0

^a Reaction conditions: 10 mmol tetrahydrofuran, 10 mmol H₂O₂ (31 wt% aqueous), 20 wt% of catalyst with respect to the substrate, temperature 343 K, reaction time 12 h.

^b Turn over frequency = number of moles of reactant converted per mole of metal per hour.


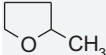
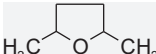
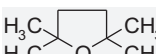

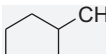

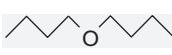
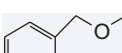
^c Mixture of products from the oxidation of C–H bonds at the β-position.

^d Ti-β was synthesized under the fluoride medium.

group selectivity, unlike the recently reported Sn-beta/H₂O₂ catalytic system, which serves as an effective chemoselective catalyst [19]. Furthermore, open-chain ethers produce carboxylic acids as the major product. Entry 8 exhibits the oxidation of open-chain symmetrical dibutylether to butyric acid, and TS-1 is more active than Ti-β. The observed results clearly indicate that the –O– link-

age in open-chain esters undergoes cleavage after the oxidation of α C–H bond to give carboxylic acids as the major product. Similarly, the oxidation of unsymmetrical benzyl methyl ether (Table 3, entry 9) leads to benzoic acid as the major product and this result is in contrast to the homogeneously catalyzed oxidation over ruthenium tetroxide, where open-chain ethers containing at least one pri-

Table 3
Oxidation of various cyclic- and open-chain ethers over TS-1 and Ti-β.^a

Entry	Substrate	Catalyst	Conversion (mol%)	H ₂ O ₂ conversion (mol %)	Lactone sel., %	Others ^b
1		TS-1	49.1	99.0	91.0	9.0
		Ti-β	44.6	97.0	90.0	10.0
2		TS-1	18.2	64.0	91.9	8.1
		Ti-β	26.0	79.0	87.0	13.0
3		TS-1	6.0	49.0	–	100
		Ti-β	9.1	62.0	–	100
4		TS-1	1.0	30.0	–	100
		Ti-β	2.3	49.0	–	100
5		TS-1	36.0	93.0	89.9	10.1
		Ti-β	32.5	96.5	88.1	11.9
6		TS-1	22.0	65.0	86.0	14.0
		Ti-β	29.7	72.5	84.4	15.6
7		TS-1	38.9	78.0	51.0	49 ^c
		Ti-β	41.2	72.9	47.5	52.5 ^c
8		TS-1	48.0	98.0	–	100 ^d
		Ti-β	42.5	99.0	–	100 ^d
9		TS-1	39.0	95.0	–	100 ^d
		Ti-β	46.8	99.0	–	100 ^d

^a Reaction conditions: 10 mmol substrate, 10 mmol H₂O₂ (31 wt% aqueous), 20 wt% of catalyst (TS-1 or Ti-β) with respect to the substrate, temperature 343 K, reaction time 12 h.

^b Mixture of α-hydroxylated ethers and other C–H oxidation products.

^c Mostly epoxidation products.

^d Carboxylic acids.

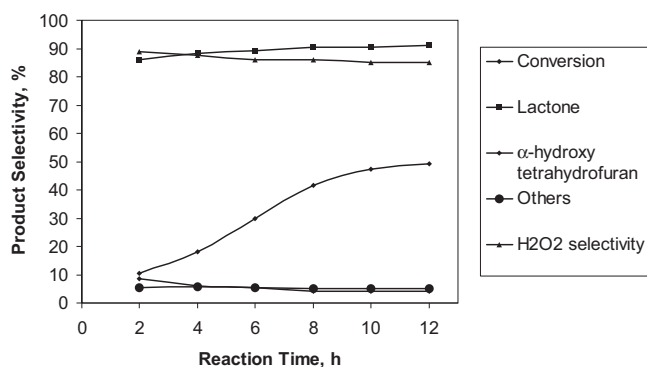


Fig. 1. Profiles for the product distribution with time in the oxidation of tetrahydrofuran over TS-1/H₂O₂.

mary alkyl group can be oxidized to the corresponding carboxylic esters [15]. In the case of oxidation of bulky benzyl methyl ether Ti-β exhibits better activity than TS-1, probably the diffusion of reactants may play a dominant role in controlling the activity of medium-pore TS-1. The observed results of various cyclic ethers suggest that TS-1 is more active and selective catalyst for less bulky substrates, whereas Ti-β shows better activity for bulky molecules due to the availability of large void-space around the active Ti sites.

3.3. Effect of substrate to H₂O₂ molar ratio and reaction time

The oxidation of tetrahydrofuran has been carried out over TS-1 at different conversion levels by changing the amount of oxidant in order to get more information on various products distribution. Table 4 shows the product distribution and as expected, the conversion increases with the amount of H₂O₂ (entries 1–5). The observed results suggest that at low substrate to H₂O₂ mole ratio, the intermediate α-hydroxy tetrahydrofuran is formed in appreciable amounts (8.1%, entry 1). However, the concentration of α-hydroxy tetrahydrofuran decreases (due to further oxidation to γ-butyrolactone) to certain extent with increase in substrate to H₂O₂ molar ratio. Moreover, the lactone selectivity is not changed significantly for up to equimolar ratio of substrate/H₂O₂. However, use of H₂O₂/substrate molar ratio of 2 (entry 5), conversion level increased but the selectivity for lactone decreased to 82.5%. This observation indicates that the titanasilicate/H₂O₂ system is somewhat less efficient to that of the Sn-beta/H₂O₂ catalytic system, where the ketone is selectively converted to the corresponding lactone with high selectivity in the range of 99% with >95% conversion.

Fig. 1 displays the effect of reaction time on conversion and selectivity of the various products formed towards the oxidation of tetrahydrofuran over TS-1/H₂O₂ system. The conversion increases with time as expected, and the selectivity of lactone increases from 85.7 to 91.0% from 2 h to 12 h. The selectivity for γ-butyrolactone increases mainly at the expense of α-hydroxy tetrahydrofuran, which is further oxidized to give more stable lactone as the main product. In the beginning, α-hydroxy tetrahydrofuran is formed in considerable amounts as observed in the case of low H₂O₂ concentration. However, the selectivity of side products also increases during the course of reaction, accounting for the oxidation of C–H bond at different positions on the tetrahydrofuran ring.

3.4. Reusability of various titanosilicates

The activity of various used titanosilicates for the oxidation of tetrahydrofuran is shown in Fig. 2. The titanosilicates were reactivated at 623 K for 5 h under the air and reused again under the similar experimental conditions using equimolar amounts of substrate/H₂O₂. The activity of the catalysts decreases with the

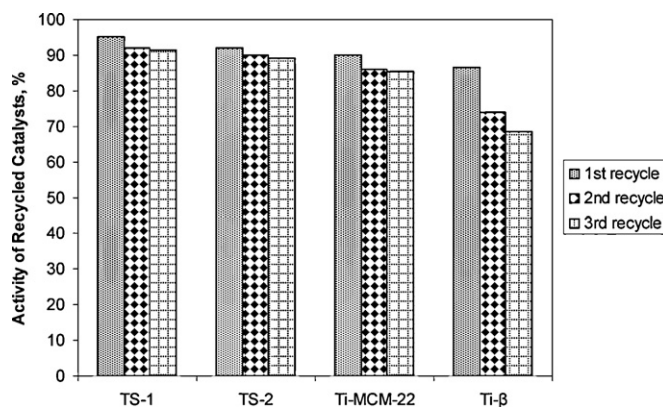


Fig. 2. The activity of various titanosilicates in three successive liquid phase catalytic recycles for the oxidation of tetrahydrofuran.

number of recycles and TS-1 showed best activity after three successive reuses (91.3%). Other medium-pore titanosilicates, TS-2 as well as Ti-MCM-22 also shows good activity of 89.0 and 86.0%, respectively. However, the activity of large-pore Ti-β was reduced by 31.5% on third reaction cycle under similar experimental conditions. The carbon content of used Ti-β estimated by CHN analysis was found to be 1.9%, which was also highest among the titanosilicates studied here. Furthermore, the chemical analysis of the solution obtained after dissolution of the framework indicated the presence of mainly lactone, α-hydroxy tetrahydrofuran and small amount of higher molecular weight products in addition to Ti, Si and O. The decrease in activity may be due to the partial leaching of framework titanium by interaction of these molecules as well as action of H₂O₂ on the Ti^{IV} active sites [33–36]. Observed Si/Ti ratios of TS-1, TS-2, Ti-MCM-22, and Ti-β increased to 45.3, 64.0, 58.5, and 64.0, respectively, after three successive reuses.

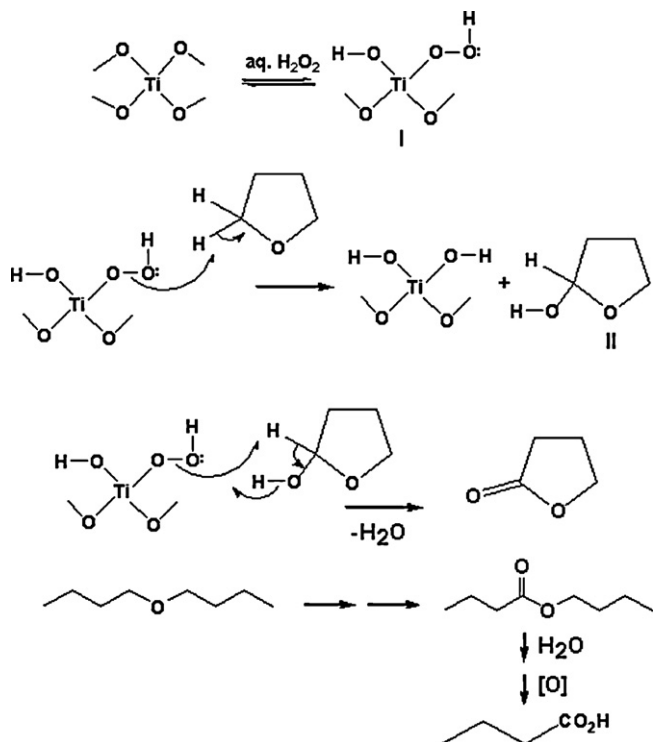
3.5. Reaction pathways

The product distribution for the oxidation of tetrahydrofuran over titanosilicates with respect to reaction time and substrate/H₂O₂ molar ratio suggests that γ-butyrolactone is probably formed via α-hydroxy tetrahydrofuran. Fig. 1 revealed the existence of an appreciable amount of the intermediate α-hydroxy ether, which decreased gradually as the reaction is progressed. In Scheme 2 we have proposed possible reaction mechanism involved in this oxidation process. Here, the reaction involves the initial oxidation of activated C–H bonds of the –CH₂ groups α to –O– group to give α-hydroxy ethers. This is followed by further attack of titaniumhydroperoxo species (I) to the C–H bond of the α-carbon atom of the α-hydroxy ethers leading to the oxidation to lactones in the case of cyclic ether. Further oxidation of α-hydroxy tetrahydrofuran (Scheme 2, II) is favored due to the presence of more activated C–H bond compared to tetrahydrofuran leading to more stable lactone, γ-butyrolactone. On the other hand for open-chain ethers like dibutylether, α-hydroxy ethers formed at the initial stage undergoes further oxidation to ester in the presence of titanium hydroperoxo species. This would be followed by hydrolysis and oxidation to yield butyric acid. Formation of benzoic acid as the major product in the oxidation of benzyl methyl ether (Table 3, entry 9) supports the initial oxidation of methylene carbon and followed by oxidative cleavage mechanism as proposed in Scheme 2. However, one cannot completely ignore the possibility of radical oxidations with hydrogen peroxide, where a metal-hydroperoxide [32–35] appears as an intermediate, which easily dehydrates to carbonyl compound by heating during either under the reaction conditions or purification processes such as distillation and/or estimation through GC. However, similar to other

Table 4
Effect of substrate to H₂O₂ molar ratio over TS-1.^a

Entry	Substrate/H ₂ O ₂ mole ratio	Conversion (mol%)	H ₂ O ₂ conversion, %	Product selectivities (%)		
				γ-Butyrolactone	α-Hydroxy tetrahydrofuran	Others
1	4	10.9	59.0	88.0	8.1	2.8
2	3.3	14.6	68.5	91.5	5.4	3.6
3	2	27.3	81.0	90.6	4.5	4.9
4	1	49.1	99.0	91.0	3.6	5.4
5	0.5	61.5	96.0	82.5	5.5	12.0

^a Reaction conditions: 10 mmol tetrahydrofuran, 20 wt% of catalyst (TS-1, Si/Ti=42.1) with respect to the substrate, temperature 343 K, reaction time 12 h.



Scheme 2. Proposed mechanistic pathways for the oxidation of ethers over titanasilicate/H₂O₂ system.

oxidation reactions catalyzed by titanium silicates, it is highly likely that, the oxidation of ethers to lactones would also be facilitated by titanium-hydroperoxo complexes formed by the interaction of Ti^{IV} species with H₂O₂ [33]. Furthermore, since titanium-hydroperoxo complexes being mild Brönsted acidic, could promote the cleavage of –O– linkage to produce carboxylic acid in the case of open-chain ethers. A similar mechanism would be applicable for the oxidation over the other metallosilicates/H₂O₂ catalytic system under investigation.

4. Conclusions

The titanasilicates can be used as heterogeneous catalyst for the oxidation of ethers to lactones or carboxylic acids in moderate to good yields in the presence of dilute aqueous H₂O₂ as oxidant. The intrinsic activity of medium-pore TS-1 was found to be higher over the TS-2, Ti-MCM-22, and Ti-β. Tetrahydrofuran exhibited the best reactivity than the other cyclic ethers investigated under the present study. The activity of substituted tetrahydrofurans decreased in the order: mono-α- > di-α, α'- > tetra-α, α, α', α'-substitution. Steric hindrance and geometrical constraints at reaction sites influence the activity of mono- and di-substituted

tetrahydrofurans, whereas tetra-α, α, α', α'-substituted compound exhibited no activity due to lack of α C–H bond. Dihydropyran containing olefinic functions produced a large amount of side products via epoxidation of –C=C– bond in addition to α C–H oxidation of ether. The distribution of products with reaction time and H₂O₂ concentration revealed α-hydroxy ethers are the initial reaction product, which is transformed to lactone as the final product. The oxidation of both symmetrical and unsymmetrical open-chain ethers produced carboxylic acids as the major product through oxidative cleavage. Further, TS-1 showed excellent recycling efficiency than the other microporous titanasilicates.

References

- [1] M. Taramasso, G. Perego, B. Notari, U.S. Patent 4,410,501, 1983.
- [2] J.S. Reddy, R. Kumar, P. Ratnasamy, Appl. Catal. 58 (1990) L1.
- [3] A. Tuel, Y.B. Taarit, Zeolites 15 (1995) 164.
- [4] T. Blasco, M.A. Cambor, A. Corma, P. Esteve, J.M. Guil, A. Martinez, J.A. Perdigon-Melon, S. Valencia, J. Phys. Chem. B 102 (1998) 75.
- [5] W. Peng, T. Tatsumi, T. Komatsu, T. Yashima, Chem. Lett. (2000) 774.
- [6] W. Fan, Y. Kubota, T. Tatsumi, ChemSusChem 1 (2008) 175–178.
- [7] P.T. Tenev, M. Chibwe, T.J. Pinnavaia, Nature 368 (1994) 321–324.
- [8] D. Chandra, S.C. Laha, A. Bhaumik, Appl. Catal. A: Gen. 342 (2008) 29–34.
- [9] A. Bhaumik, S. Samanta, N.K. Mal, Micropor. Mesopor. Mater. 68 (2004) 29–35.
- [10] M. Sasidharan, A. Bhaumik, J. Mol. Catal. A: Chem. 328 (2010) 60–67.
- [11] S.L. Jain, B.S. Rana, B. Singh, A.K. Sinha, A. Bhaumik, M. Nandi, B. Sain, Green Chem. 12 (2010) 374–377.
- [12] R.A. Sheldon, R.S. Downing, Appl. Catal. A: Gen. 189 (1999) 163.
- [13] P. Muller, in: S. Patai (Ed.), The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues, Wiley, New York, 1980, Suppl. E, p. 469.
- [14] S.M. Kupchan, M.A. Eakin, A.M. Thomas, J. Med. Chem. 14 (1971) 1147.
- [15] M. Kaname, S. Yoshifuji, H. Sashida, Heterocycles 79 (2009) 647–658.
- [16] P.H.J. Carlsen, T. Katsuki, V.S. Martin, K.B. Sharpless, J. Org. Chem. 46 (1981) 3936.
- [17] J. Muzart, J. Mol. Catal. A: Chem. 319 (2010) 1–29.
- [18] R.A. Sheldon, J. Dakka, Catal. Today 19 (1994) 215.
- [19] A. Corma, L.T. Nemeth, M. Renz, S. Valencia, Nature 412 (2001) 423.
- [20] M. Sasidharan, Y. Kiyozumi, N.K. Mal, M. Paul, P.R. Rajamohanan, A. Bhaumik, Micropor. Mesopor. Mater. 126 (2009) 234–244.
- [21] M. Sasidharan, S. Suresh, A. Sudalai, Tetrahedron Lett. 36 (1995) 9071.
- [22] A. Thangaraj, R. Kumar, S.P. Mirajkar, P. Ratnasamy, J. Catal. 130 (1990) 1.
- [23] G. Bellussi, M.S. Rigutto, Stud. Surf. Sci. Catal. 85 (1994) 177.
- [24] J.S.T. Mambim, H.O. Pastore, C.V. Davanzo, E.J.S. Vichi, O. Nakamura, H. Vargas, Chem. Mater. 5 (1993) 166.
- [25] B. Jayachandran, M. Sasidharan, A. Sudalai, T. Ravindranathan, J. Chem. Soc. Chem. Commun. (1995) 1523.
- [26] J. Reni, M. Sasidharan, A. Sudalai, T. Ravindranathan, J. Chem. Soc. Chem. Commun. (1995) 1341.
- [27] N.V. Barhate, M. Sasidharan, A. Sudalai, R.D. Wakharkar, Tetrahedron Lett. (1996) 707.
- [28] M. Sasidharan, P. Wu, T. Tatsumi, J. Catal. 205 (2002) 332.
- [29] A. Carati, C. Flego, E.P. Massara, R. Millini, L. Carluccio, W.O. Parker Jr., G. Bellussi, Micropor. Mesopor. Mater. 130 (1999) 137.
- [30] L.J. Davis, P. McMorn, D. Bethell, P.C. Bulman Page, F. King, F.E. Hancock, G.J. Hutchings, J. Catal. 198 (2001) 319.
- [31] L.J. Davis, P. McMorn, D. Bethell, P.C. Bulman Page, F. King, F.E. Hancock, G.J. Hutchings, J. Mol. Catal. A 165 (2001) 243.
- [32] G. Bellussi, A. Carati, M.G. Clerici, G. Maddinelli, R. Millini, J. Catal. 133 (1992) 220.
- [33] A. Bhaumik, T. Tatsumi, J. Catal. 176 (1998) 305–309.
- [34] G.N. Vayssilov, Catal. Rev. Sci. Eng. 39 (1997) 209–251.
- [35] S. Mukherjee, M. Nandi, K. Sarkar, A. Bhaumik, J. Mol. Catal. A: Chem. 301 (2009) 114–117.
- [36] J. Iglesias, J.A. Melero, J. Sainz-Pardo, J. Mol. Catal. A: Chem. 291 (2008) 75–84.