One-pot synthesis of campholenic aldehyde from α-pinene over Ti-HMS catalyst II: effects of reaction conditions

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Abstract

Ti-substituted HMS catalyst has been prepared and applied as a bifunctional catalyst to the two-step conversion of α-pinene via α-pinene oxide to campholenic aldehyde using TBHP as an oxidant. The reaction mainly proceeds by a radical mechanism, leading to the formation of allylic oxidation products like verbenol and verbenone. To suppress the formation of byproducts, other oxygen sources except for the oxidant are removed from the reaction system. In the presence of water, the hydrophilic character of Ti-HMS can induce the preferential accessibility of water, resulting in the increase of intraporous water concentration and its subsequent blocking of catalytic sites. Also, in the presence of oxygen, the propagation of radicals is promoted and this leads to the formation of other side-products. After removing water and molecular oxygen, it is possible to synthesize campholenic aldehyde in one-pot over Ti-HMS catalyst. Therefore, the removal of other oxygen sources that may lead to the allylic oxidation is essential for the one-pot conversion of α-pinene to campholenic aldehyde.
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1. Introduction

Since the discovery of TS-1 [1], a great deal of research interest has been directed to the use of redox-molecular sieves as partial oxidation catalysts for the synthesis of bulk and fine chemicals [2]. The use of TS-1 is, however, limited due to its rather small pore size, so that only linear olefins are efficiently epoxidized. On the other hand, Ti-containing mesoporous molecular sieves such as Ti-MCM-41 [3] and Ti-HMS [4] have shown much better ac-

tivities than the zeolites for the oxidation of larger organic molecules that are diffusion-limited even in a large-pore zeolite of titanium Beta (Ti-Beta) [5,6], and have opened new possibilities for the production of oxygenated fine chemicals.

Terpenes are widely distributed in nature and their epoxides often serve as starting materials for the synthesis of fragrances, flavors and therapeutically active substances [7,8]. Among a number of terpenes, α-pinene is an important substance in the manufacture of a variety of synthetic aroma chemicals and its epoxide is isomerized to produce campholenic aldehyde, which is an intermediate for the sandalwood fragrance, santalol [9,10], as shown in Fig. 1. So far air oxidation of α-pinene has received a considerable

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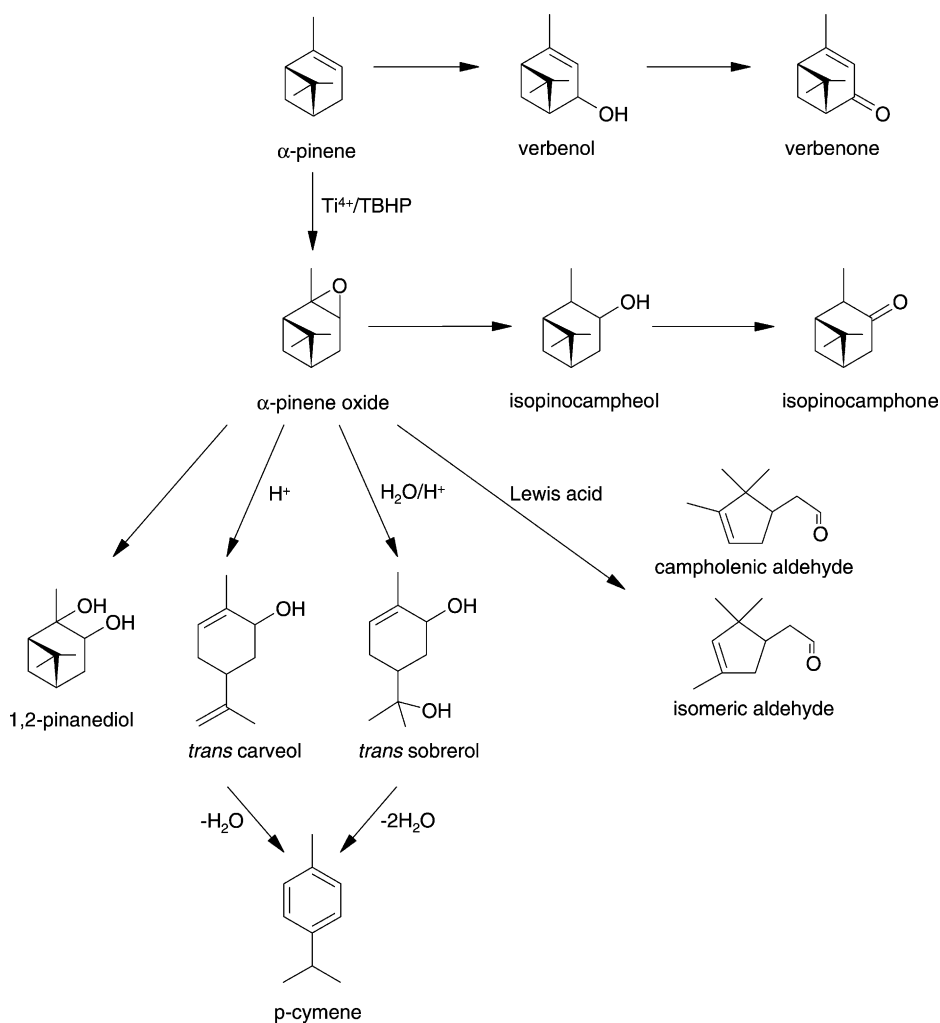
Fig. 1. Reaction network of α-pinene conversion.

attention [8]. However, this process has not been commercialized because of the formation of various side-products, extensive decomposition and polymerization [11]. The consecutive rearrangement of α-pinene oxide is facile and more than 100 products have been reported under different reaction conditions [12]. The use of mild Lewis acids favors the production of campholenic aldehyde, while Brønsted acid sites brings about the formation of trans-carveol, trans-sobrerol and p-cymene [13]. Well-known active and selective homogeneous catalysts used for this reaction are ZnCl$_2$ and ZnBr$_2$ [12]; however, rapid irre-

versible catalyst deactivation is observed with turnover numbers as low as 20 being reported [10]. Aqueous extraction of these catalysts from the reaction mixture results in a large amount of zinc-contaminated water that is environmentally unacceptable; hence alternative heterogeneous catalysts must be sought.

Although heterogeneous catalysts may be applied for the catalytic epoxidation of α-pinene, relatively few studies have been reported [14–16]. Recently, it was briefly reported that this reaction was carried out over heterogeneous catalysts prepared by grafting metallocene complexes onto mesoporous silica

[14]. Also, this reaction was tested over bifunctional titanium-mesoporous molecular sieves containing different trivalent ions such as B^{3+}, Al^{3+} or Fe^{3+} [15]. However, these authors discussed only the influence of the nature of the trivalent ion on the activity for the epoxidation of α-pinene and the selectivity toward the formation of the corresponding diol. They suggested that the additional weak acidic sites induced by the framework incorporated trivalent cation affected significantly the product distribution and favored the diol formation.

In contrast to the study of α-pinene epoxidation, the acid-catalyzed rearrangement of α-pinene oxide has been studied over various solid Lewis acids by many researchers [17–20]. In more recent years, aluminum-free zeolite titanium Beta (Ti-Beta) was applied to the rearrangement of α-pinene oxide into campholenic aldehyde [21]. This material was tested as the catalyst because its Lewis acid activity was demonstrated in the epoxidation of alkenes and the Meerwein–Ponndorf–Verley reduction of 4-*tert*-butylcyclohexanone to the corresponding *cis*-alcohol [22,23]. Ultra stable Y-zeolite with Lewis acidic extra framework alumina was also found to be an excellent catalyst for the rearrangement of α-pinene oxide to campholenic aldehyde [12,24].

It has been reported in recent years that the oxirane formed by the epoxidation of olefin is consecutively rearranged into the corresponding aldehyde or ketone on the bifunctional catalysts such as Ti-Al-Beta [25] and Ti-B-MFI [26]. However, this idea has not been tried yet in synthesizing campholenic aldehyde in one-pot starting from α-pinene. More recently, we have reported the use of Ti-HMS as a bifunctional catalyst for the one-pot conversion of α-pinene to campholenic aldehyde and thereby suggested a new route for the preparation of campholenic aldehyde [27].

It may be noticed from our previous work that each of the various oxygen sources exercised a significant influence on the reaction of α-pinene. In this study we have examined the strategy of removing various oxygen sources such as water and molecular oxygen in the one-pot synthesis of campholenic aldehyde using TBHP and investigated the effect of each oxygen source on the reaction performance, and thereby suggested the optimum condition for the one-pot synthesis of campholenic aldehyde from α-pinene.

2. Experimental

2.1. Preparation of catalysts

Ti-HMS samples were prepared following a recipe similar to that reported by Zhong et al. [4]. First, a solution was prepared by mixing tetraethylorthosilicate (TEOS, Aldrich, 98% solution) and titanium(IV) butoxide (Aldrich, 99% solution) dissolved in ethanol. Then a second solution was prepared by mixing dodecylamine (DDA, Aldrich, 98%), distilled water, and HCl (35%). The solution was stirred vigorously and the first solution was slowly added over a period of ca. 30 min. The molar gel composition of the final reaction mixture was $SiO_2:xTiO_2:0.2$ DDA:9 EtOH:0.02 HCl:160 H_2O, where x takes a value between 0.02 and 1. The substrate mixture was aged at room temperature under vigorous stirring for about 24 h to give a crystalline product. The white solid obtained was recovered by filtration, extracted with ethanol for 2 h, washed several times with distilled water, and dried at 373 K in an oven. Subsequently, the as-synthesized products were calcined in air at 823 K for 5 h to remove the surfactant and organic compounds trapped within the framework.

2.2. Characterization of catalysts

The solids were characterized by X-ray diffraction on a Rikagu D/MAX-A diffractometer using Cu Kα radiation. Surface area measurements were obtained on an ASAP-2000 apparatus following the BET procedure. Pore size distribution was obtained using nitrogen as adsorbate and following the Barrett Joyner Halenda (BJH) method. The chemical composition of the calcined sample was measured by induced-coupled plasma (ICP) analysis using a Varian Spectra A-10 plus apparatus. UV-Vis spectra were obtained with a Perkin-Elmer λ20 spectrometer.

2.3. Catalytic reactions

Catalytic reactions were carried out in a round-bottomed flask under stirring and reflux. The reaction temperature was maintained at the desired temperature using a temperature controlled water bath. In a typical reaction procedure, 30 ml of acetonitrile (HPLC grade) as solvent, 5 mmol of α-pinene (ACROS), 5 mmol of
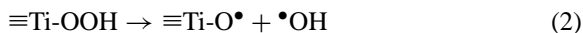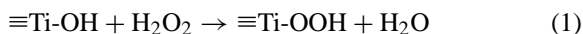
tert-butyl hydroperoxide (TBHP; Aldrich) and 100 mg of *m*-xylene as an internal standard were put together into a flask and magnetically stirred. A 0.1 g of the catalyst, dried at 473 K for 3 h, was added in one lot. Liquid samples of this suspension were taken out at successive times with a filtering syringe and analyzed by an HP5890 gas chromatography equipped with an FID and an HP INNOWAX (crosslinked polyethylene glycol, 60 m × 0.32 mm × 0.5 μm) capillary column. Identification of reaction products was performed by mass spectrometry using standard compounds. In some experiments, the reaction was carried out under nitrogen atmosphere or TBHP (70 wt.% in water) was repeatedly dried by $MgSO_4$ to remove water completely. After filtration, the dried TBHP was stored with 3A zeolite. It was observed that leaching of Ti was minimal after the reaction.

3. Results and discussion

3.1. Reaction mechanism

The catalytic reaction of α-pinene over Ti-HMS catalyst was carried out with 5 mmol of oxidant, 5 mmol of substrate, and 0.1 g of catalyst. Aqueous solution of 70 wt.% TBHP was used as the oxidant in the reaction. The reaction performance is shown in Fig. 2. Various oxygenated products were detected in addition to α-pinene oxide and campholenic aldehyde.

The reaction performance observed can be explained on the basis of the reaction network depicted in Fig. 1. The catalytic oxidative transformation of olefins proceeds by both the nonradical and radical mechanisms [28]. By the mechanism involved with radicals, large amounts of allylic oxidation products, verbenol and verbenone, were formed in the reaction mixture. These are compounds that have similar characters to cyclohexenol and cyclohexenone in the epoxidation of cyclohexene, which are formed by the radicals originating from the decomposition of peroxo titanium species formed by reaction of H_2O_2 with the titanium sites on the catalyst [29–31]:

$$\equiv Ti\text{-}OH + H_2O_2 \rightarrow \equiv Ti\text{-}OOH + H_2O \quad (1)$$

$$\equiv Ti\text{-}OOH \rightarrow \equiv Ti\text{-}O^\bullet + {}^\bullet OH \quad (2)$$

$$\equiv Ti\text{-}O^\bullet + H_2O \rightarrow \equiv Ti\text{-}OH + OH^\bullet \quad (3)$$

On the other hand, the direct epoxidation route proceeds in the absence of radicals and this produces α-pinene oxide observed in our results. According to our experimental result, the reaction yielded more allylic oxidation products than epoxides. This indicates that the radical-mediated reaction is dominant over the direct epoxidation.

As mentioned above, the epoxide formed is subsequently rearranged by the Brønsted and/or Lewis acid sites present in the catalysts to various isomerized products such as 1,2-pinanediol, *trans*-carveol, *trans*-sobrerol, *p*-cymene, campholenic aldehyde and its isomeric aldehyde [13], as shown in Fig. 1. Of these rearranged products, *trans*-carveol, *trans*-sobrerol, and *p*-cymene were observed but their amounts were negligibly small, whereas 1,2-pinanediol, campholenic aldehyde, and its isomeric aldehyde were formed in substantial amounts, enough to be analyzed, under our reaction conditions over Ti-HMS catalyst. The formation of campholenic aldehyde indicates that Lewis acid sites are present in Ti-substituted mesoporous molecular sieves, which was observed in the previous work [27].
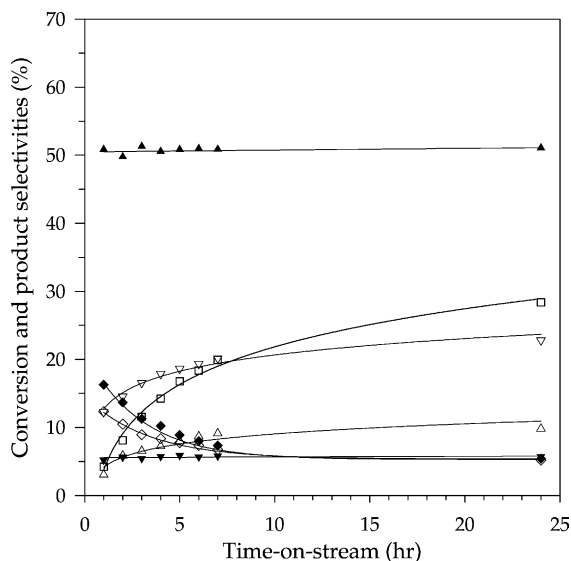

Fig. 2. Results of the reaction of α-pinene with TBHP before drying over Ti-HMS catalyst under air atmosphere as a function of time-on-stream: conversion of α-pinene (□) and product selectivities to α-pinene oxide (◇), campholenic aldehyde (▽), isomeric aldehyde (△), pinanediol (◆), verbenol (▼) and verbenone (▲), respectively. Reaction conditions: 0.1 g catalyst, 5 mmol α-pinene, 5 mmol TBHP, 30 ml acetonitrile, 350 K.

It is, therefore, desired to suppress the formation of byproducts by the radical mechanism. For this purpose, we should evaluate the influence of various oxygen sources in the catalytic reaction system. In the present reaction system, there are three different kinds of oxygen source, i.e. the oxidant, water contained in the oxidant, and oxygen existing within the reaction vessel. In the following sections, we report our effort to remove oxygen sources other than the oxidant.

3.2. Removal of water contained in the oxidant

In the reaction experiment, we used 70 wt.% TBHP solution in water as the oxidant. A large amount of water is contained in this substance because the molar ratio of TBHP to water is 32/68. Before preparing the reaction mixture, TBHP in water was dried by $MgSO_4$ and then used in the reaction.

The reaction results are presented in Fig. 3. In the beginning of the reaction, pinanediol and verbenol were not formed at all and verbenone was formed in a moderate amount. As the reaction proceeded, both
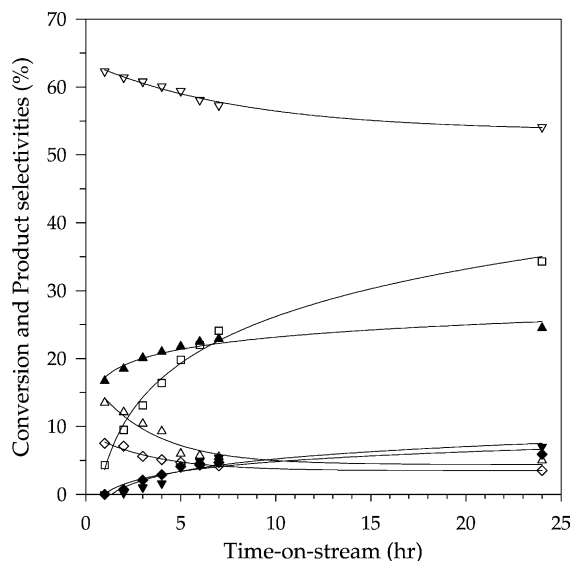

Fig. 3. Results of the reaction of α-pinene with TBHP after drying by $MgSO_4$ over Ti-HMS catalyst under air atmosphere as a function of time-on-stream: conversion of α-pinene (□) and product selectivities to α-pinene oxide (◇), campholenic aldehyde (▽), isomeric aldehyde (△), pinanediol (◆), verbenol (▼) and verbenone (▲), respectively. Reaction conditions are the same as in Fig. 2.

α-pinene oxide and its rearranged aldehyde slowly decreased. After 24 h of reaction time, other byproducts, pinanediol and verbenol, were observed and the selectivity to verbenone reached the level of about 25%. When compared with the results obtained in the presence of both water and oxygen, the conversion of α-pinene increased only slightly, but the selectivity to verbenone decreased to one-half. A slight increase of conversion can be attributed to the relatively easy accessibility of substrate to the catalyst surface, which was induced by the removal of water. Also, production of radicals is reduced and this is responsible for the decrease in the selectivity to verbenone.

3.3. Removal of oxygen existing in the reactor

As a donor of oxygen, we can think of the molecular oxygen existing in the reaction vessel. This kind of oxygen may allow the autoxidation of olefins to take place in the catalytic reaction system. Autoxidation of α-pinene has been carried out by employing a wide spectrum of homogeneous catalysts, ranging from metal-oxo types to electron-transfer ones [32]. More recently, the role of molecular oxygen in the epoxidation of cyclohexene over Ti/SiO_2 catalysts has been briefly discussed [33]. According to this report, the total amount of products formed is approximately three times larger than that formed in the absence of molecular oxygen. Therefore, it is expected that the molecular oxygen can initiate the radical mechanism under the reaction conditions of this study.

Before the reaction, the reaction mixture was purged with nitrogen for 30 min to remove molecular oxygen existing inside the reactor. TBHP was not dried by $MgSO_4$ in this case. As presented in Fig. 4, the reaction performance and the product selectivities are different from those of the previous experimental results. The conversion of α-pinene shows a substantial decrease, which may be caused by the water contained in TBHP that blocks the catalytic sites. At the initial stage of reaction, the formation of verbenone was hardly observed and especially among several rearranged products, only campholenic aldehyde was detected by gas chromatography. This indicates that, at the initial stage of reaction, all of α-pinene is epoxidized by the reaction between titanium active sites and the oxidant, and subsequently rearranged into isomeric aldehyde by the action of the Lewis acidic

character of Ti. Also, the fact that verbenone was not formed at all is a direct evidence that molecular oxygen makes the radical mechanism propagate.

In order to investigate further the effect of oxygen, we conducted an additional experiment without catalyst. The result of blank test under the same reaction
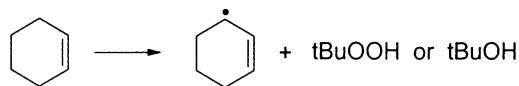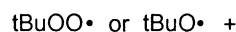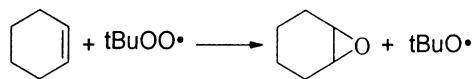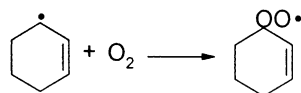
conditions shows that allylic oxidation occurred with oxidant and/or oxygen, resulting in the formation of both verbenol and verbenone. This result indicates that molecular oxygen promotes not the epoxidation actually, but the propagation of the radicals produced, as depicted in the scheme presented below. Without oxygen, reactions (6)–(8) cannot proceed and thus allylic oxidation products will not be formed under such conditions.

Nevertheless, verbenone was observed after 5 h of time-on-stream. This means that a small amount of O_2 was generated within the reactor. In other words, it is considered that the removal of oxygen by N_2 purge for 30 min may not be sufficient to generate
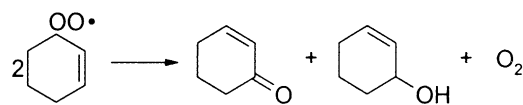
N_2 atmosphere. For complete removal of molecular oxygen, the reactor should be purged during the entire course of reaction.
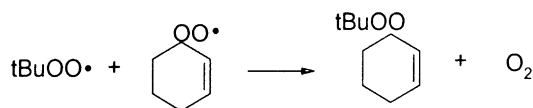
$$+ \text{ tBuOO} \bullet \longrightarrow \text{O} + \text{tBuO}\bullet \tag{4}$$

$$\text{tBuOO}\bullet \text{ or tBuO}\bullet + \longrightarrow + \text{ tBuOOH or tBuOH} \tag{5}$$

$$\bullet + O_2 \longrightarrow \text{OO}\bullet \tag{6}$$

$$2 \, \text{OO}\bullet \longrightarrow \text{O} + \text{OH} + O_2 \tag{7}$$

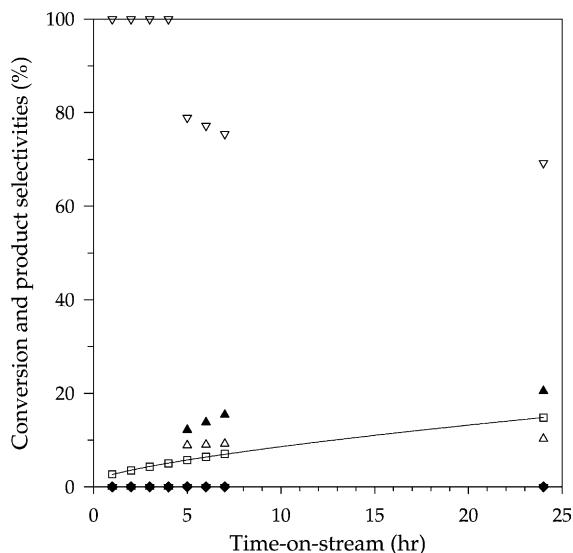$$\text{tBuOO}\bullet + \text{OO}\bullet \longrightarrow \text{tBuOO} + O_2 \tag{8}$$

Fig. 4. Results of the reaction of α-pinene with TBHP before drying over Ti-HMS catalyst under N_2 atmosphere as a function of time-on-stream: conversion of α-pinene (□) and product selectivities to α-pinene oxide (◇), campholenic aldehyde (▽), isomeric aldehyde (△), pinanediol (◆), verbenol (▼) and verbenone (▲), respectively. Reaction conditions are the same as in Fig. 2.
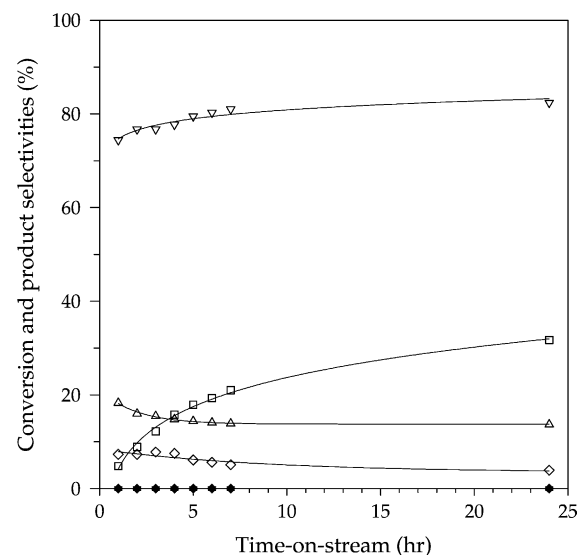
Fig. 5. Results of the reaction of α-pinene with TBHP after drying by $MgSO_4$ over Ti-HMS catalyst under N_2 atmosphere as a function of time-on-stream: conversion of α-pinene (□) and product selectivities to α-pinene oxide (◇), campholenic aldehyde (▽), isomeric aldehyde (△), pinanediol (◆), verbenol (▼) and verbenone (▲), respectively. Reaction conditions are the same as in Fig. 2.

3.4. Simultaneous removal of oxygen sources

Evidently, it is desired to remove both water and molecular oxygen from the reaction system. After TBHP was dried by $MgSO_4$ prior to use, the oxyfunctionalization of α-pinene was carried out over Ti-HMS catalyst at 350 K under nitrogen atmosphere generated by N_2 purge throughout the reaction and the reaction results are presented in Fig. 5. Clearly, the catalytic activity turns out to be improved in all aspects. After the simultaneous removal of water and molecular oxygen, the conversion of α-pinene increased slightly and only two products, α-pinene epoxide and its isomerized aldehyde, were observed. This indicates that the one-pot procedure for the transformation of α-pinene via α-pinene oxide into campholenic aldehyde was accomplished successfully. Consequently, the removal of all the oxygen sources, which may be responsible for the allylic oxidation, is essential for the one-pot conversion of α-pinene to campholenic aldehyde.

4. Conclusions

In this work, we have demonstrated that it is possible to realize the one-pot synthesis of campholenic aldehyde from α-pinene. This reaction scheme requires a catalyst with both the epoxidative and Lewis acidic functions. It is shown that Ti-substituted mesoporous molecular sieves (Ti-HMS) can be applied to the conversion of α-pinene using TBHP.

To suppress the formation of byproducts by the radical mechanism in the oxyfunctionalization of α-pinene, it is required to remove water contained in the oxidant and/or molecular oxygen existing within the reaction vessel. With water removed, the catalyst having hydrophilic nature of the surface facilitates the access of reactants to the active sites, and this gives rise to the increase of α-pinene conversion. Also, the radicals formed by reactions (2) and (3) can be propagated, leading to the formation of allylic oxidation products under air atmosphere. Consequently, the radical-mediated reaction must be suppressed by the removal of oxygen. After removing water and molecular oxygen, only two products, α-pinene oxide and its isomerized aldehyde, were formed. This indicates that the one-pot procedure for the transformation of α-pinene into campholenic aldehyde can be accomplished by removing other oxygen sources that may promote allylic oxidation.

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