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Redox-mesoporous molecular sieve as a bifunctional catalyst for the one-pot synthesis of campholenic aldehyde from α-pinene

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Abstract

Ti-HMS catalyst has been used as a bifunctional catalyst in the one-step conversion of α-pinene to campholenic aldehyde, i.e. with purification treatment, one-pot synthesis of campholenic aldehyde could be accomplished by using Ti-substituted mesoporous molecular sieves in which Lewis acid sites were present. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Conventional homogeneously catalyzed processes produce a large amount of waste upon the removal of catalyst from the reaction system. To overcome such a drawback, new heterogeneous catalytic systems have been extensively investigated [1–3]. One of such schemes is the 'one-pot' reaction procedure, which means that a chemical conversion consisting of a number of sequential reactions is achieved in a single reaction step [4]. Especially, in the field of fine chemicals, most of the processes are still homogeneously catalyzed and thus, it is required to overcome the well-known limitations of homogeneous catalysis by applying better alternatives.

Terpenes are widely distributed in nature and their epoxides often serve as starting materials for the synthesis of fragrances, flavors and therapeutically active substances [5,6]. Among a number of terpene derivatives, α-pinene epoxide (**2**) is rearranged into campholenic aldehyde (**3**), an intermediate for the sandalwood fragrance santalol [7]. The most active and selective homogeneous catalysts used in this reaction are $ZnCl_2$ and $ZnBr_2$, both of which are typical of Lewis acid catalysts [8]. However, aqueous extraction of these catalysts from the reaction system results in a large volume of zinc-contaminated water that is environmentally unacceptable.

Therefore, if a single solid catalyst bears both epoxidative and Lewis acidic functions, it would be possible to convert α-pinene via α-pinene oxide into campholenic aldehyde in one-pot reaction (cf. Scheme 1). In recent years, titanium-substituted molecular sieves are known to have the Lewis acidic character, which was demonstrated by the epoxidation of alkenes and the Meerwein–Ponndorf–Verley reduction of 4-*tert*-butylcyclohexanone to the corresponding *cis*-alcohol [9,10]. In this respect, an HMS material containing Ti^{4+} as oxidation and Lewis acid sites is shown here to transform α-pinene to campholenic aldehyde in one-pot.

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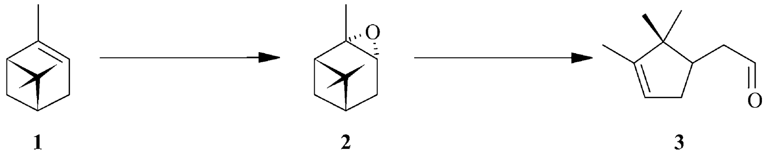


Scheme 1.

2. Experimental

2.1. Preparation of catalysts

Ti-HMS sample was prepared following a recipe similar to that reported by Zhong and co-workers [11]. First, a solution was prepared by mixing tetraethyl orthosilicate (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 to this solution, the first solution was slowly added over a period of ca. 30 min. The molar gel composition of the final reaction mixture was SiO_2:0.1 TiO_2:0.2 DDA:9 EtOH:0.02 HCl:160 H_2O. The substrate mixture was aged at room temperature under vigorous stirring for about 24 h to obtain 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 in an oven at 373 K. Subsequently, the as-synthesized products were calcined in air at 823 K for 5 h to remove the surfactant and organic compounds located within the framework.

2.2. Characterization

X-ray diffraction patterns were recorded between 1 and 10° on a Cu Kα radiation ($\lambda = 1.5406$ Å). The UV–VIS spectra were obtained in the reflection mode using a Varian CARY 3E double beam spectrometer in the range of 190–800 nm. For Brunauer–Emmett–Teller (BET) analysis, N_2 adsorption/desorption isotherms were collected on an ASAP-2010 apparatus. Samples were evacuated at 523 K overnight prior to analysis. The pore size and its distribution were calculated by the Barrett–Joyner–Halenda (BJH) method.

Self-supporting 15 mg catalyst wafers (diameter 13 mm) were pretreated in situ at 573 K in a glass cell fitted with KBr windows and high-vacuum stopcocks. Afterwards, the cell was evacuated to a pressure of approximately 10^{-3} Torr and cooled to room temperature in vacuum. Then, samples were exposed to pyridine at 20 Torr for 10 min. The spectra were recorded after evacuation to the base pressure under increasing mode of evacuation temperature from 323 to 573 K. Background spectrum was recorded in advance at the same temperature as the sample and subtracted from the sample spectrum. The spectra were recorded on a Nicolet Impact 410 Fourier-transform spectrometer with a resolution of 4 cm^{-1} and scan number of 100.

2.3. Reaction experiments

Catalytic reactions were carried out in a round-bottomed flask under stirring and reflux at 350 K. In a typical reaction procedure, acetonitrile (30 ml) as a solvent, catalyst (100 mg), α-pinene (5 mmol), *tert*-butyl hydroperoxide (TBHP; 5 mmol) and *m*-xylene (0.1 ml) as an internal standard were put in a flask and magnetically stirred. Liquid samples of this suspension were extracted by a filtering syringe at successive times and analyzed by FID in an HP5890 gas chromatography fitted with HP INNOWAX (crosslinked polyethylene glycol, 60 m × 0.32 mm × 0.5 μm) capillary column. Identification of reaction products was performed by GC–MS and using standard compounds.

3. Results and discussion

3.1. Catalyst characterization

The calcined Ti-HMS sample showed quite a narrow pore size distribution around 38 Å and

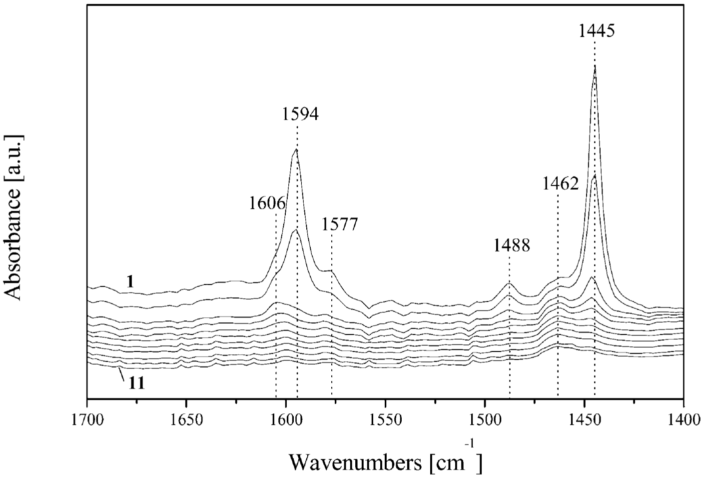


Fig. 1. FTIR spectra of Ti-HMS upon adsorption of pyridine. The curves 1–11 represent the spectra obtained at different temperatures and are arranged in such a way that the corresponding temperature increases successively from 323 to 573 K at an interval of 25 K. The last spectrum was obtained by evacuating the sample at 573 K for 30 min.

Barrett–Joyner–Halenda (BJH) surface area of 1200 m^2 g^{-1}, which were comparable to the ones previously reported for these samples [12]. The isomorphous substitution of Si by Ti in HMS framework was confirmed by powder X-ray diffraction (XRD) and FTIR characterization. The UV–VIS spectrum of the sample also showed bands at 210–230 nm which indicate that Ti is in a 4–6 coordinations.

The Lewis acidity of the sample was recognized by the adsorption of pyridine and IR spectroscopy. Pyridine, which is more basic than ammonia, was used as the probe molecule for analysis of the surface acidity of Ti-substituted mesoporous materials by FTIR spectroscopy [13–15]. In Fig. 1, the infrared spectra of the adsorbed pyridine are shown in the region of 1700–1400 cm^{-1} in vacuum subjected to different thermal treatments in the temperature range of 323–573 K. Here, all the spectra exhibit bands due to hydrogen bonded pyridine (1445 and 1594 cm^{-1}), strong Lewis bound pyridine (1462 cm^{-1}), weak Lewis bound pyridine at 1577 cm^{-1}, and a band at 1488 cm^{-1} which can be assigned to pyridine associated with both Brønsted and Lewis sites. The positions of these bands are consistent with the results as previously reported for Si-MCM-41 [14] and Ti-HMS [15]. However, pyridium ions ring vibration bound to Brønsted acid sites at about 1546 and 1639 cm^{-1} is not observed for Ti-HMS materials [14,15], and this indicates that no Brønsted acid sites are present. Therefore, the band at 1488 cm^{-1} can be related only to Lewis acid sites.

With thermal treatment from 323 to 573 K, the peak intensity of pyridine coordinated to Lewis acid sites at 1462, 1488, and 1577 cm^{-1} decreased consid-

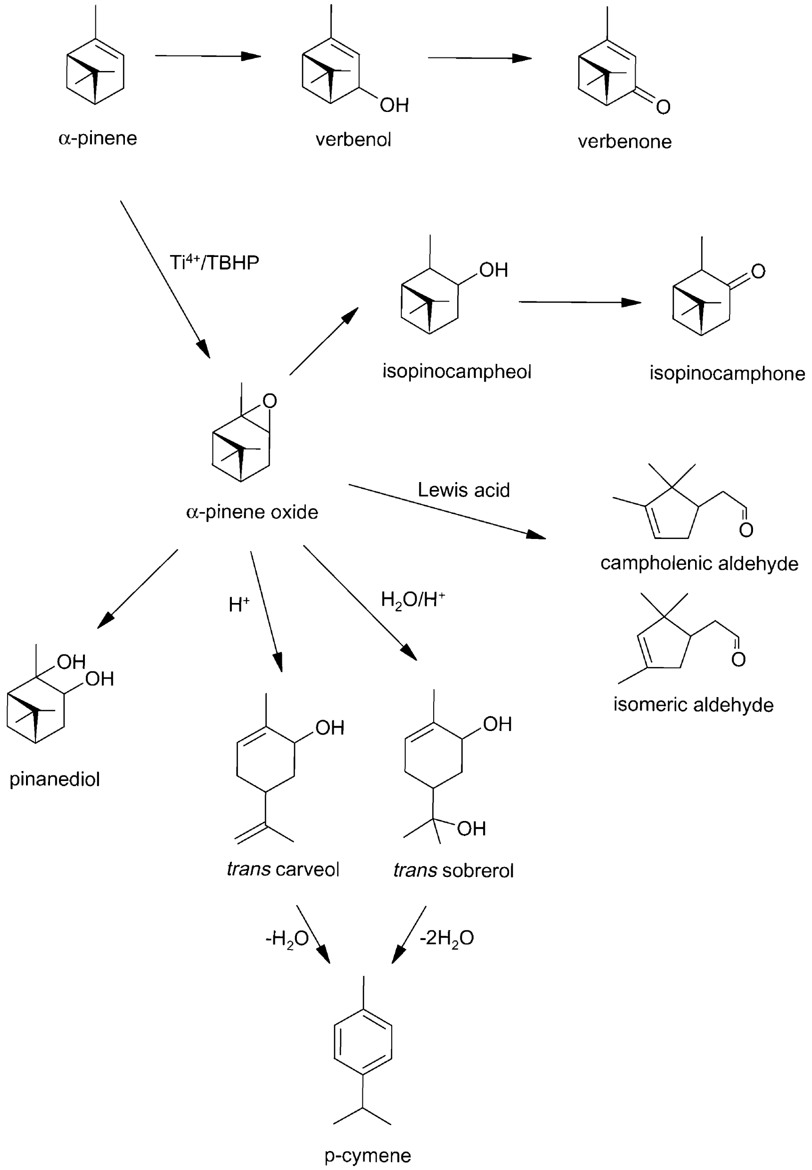
Table 1
Experimental results of Ti-HMS catalyzed reaction of α-pinene with TBHP[a]

	Condition A[b]	Condition B[c]
	28.4	31.7
Selectivity (%)		
α-Pinene oxide	5.2	3.9
Campholenic aldehyde	22.8	82.4
Isomeric aldehyde	9.8	13.7
1,2-Pinanediol	5.4	0
Verbenol	5.7	0
Verbenone	51.1	0

[a] Reaction conditions: α-pinene (5 mmol), TBHP (5 mmol), 0.1 g catalyst, acetonitrile (30 ml), internal standard (0.1 ml), 350 K, 24 h.

[b] TBHP was not dried by $MgSO_4$ and the experiment was conducted under air atmosphere.

[c] TBHP was dried by $MgSO_4$ and the experiment was conducted under N_2 atmosphere.



Scheme 2.

erably; nevertheless, small amounts of Lewis bound pyridine still remained at 473 K and 10^{-4} Torr vacuum. This indicates that moderate Lewis acid sites are present in the Ti-HMS sample. As shown in Scheme 1, therefore, α-pinene oxide can be rearranged into campholenic aldehyde by Lewis acid sites of Ti-HMS.

3.2. One-pot synthesis of campholenic aldehyde from α-pinene over Ti-HMS

We first carried out the catalytic reaction of α-pinene over Ti-HMS catalyst with 70 wt.% TBHP in water without purification treatment (condition A) and the results are presented in Table 1. Here, various oxygenated products were observed in addition to α-pinene oxide and campholenic aldehyde. In general, the catalytic oxidative transformation of olefins proceeds by both nonradical and radical mechanisms [16]. Large amounts of allylic oxidation products such as verbenol and verbenone were formed in the reaction mixture by the latter mechanism. These compounds have similar characters to cyclohexenol and cyclohexenone in the epoxidation of cyclohexene. These products are formed by the radicals originated from decomposition of peroxo titanium species obtained by the reaction of H_2O_2 with the titanium sites of the catalyst [17]. On the other hand, direct epoxidation proceeds in the absence of radicals to produce α-pinene oxide observed in our experiment. According to our experimental result, the reaction yielded more allylic oxidation products than epoxides. This indicates that the radical-mediated reaction is dominant over direct epoxidation.

It is recognized that Brønsted and/or Lewis acid sites present in the catalysts subsequently rearrange α-pinene oxide into various isomerized products such as pinanediol, *trans*-carveol, *trans*-sobrerol, campholenic aldehyde and its isomeric aldehyde [18], as shown in Scheme 2. Of these rearranged products, only pinanediol and campholenic aldehyde were observed under the present reaction conditions over Ti-HMS catalyst. Taking into account the formation of campholenic aldehyde, one can speculate that Lewis acid sites are present in Ti-substituted mesoporous molecular sieves. These sites were found to exist by FTIR adsorption experiments of pyridine. This information suggests the possibility of one-pot synthesis of campholenic aldehyde from α-pinene over Ti-HMS material.

To suppress the formation of byproducts by the radical mechanism in the epoxidation of α-pinene, it is required to remove other oxygen sources in the reaction system except for the oxidant [19]. Potential oxygen sources other than the oxidant would be the water contained in the oxidant and the molecular oxygen existing within the reaction flask. First, water may compete with the reactant and be adsorbed more preferentially than the hydrophobic olefins due to the hydrophilic nature of Ti-substituted mesoporous molecular sieves [20]. This indicates that Ti-substituted materials may not be active in the epoxidation of olefins if water is present. In the second place, the molecular oxygen existing within the reaction flask can cause autoxidation of olefins in catalytic systems. More recently, a brief report has been published on the role of molecular oxygen in the epoxidation of cyclohexene over Ti/SiO_2 catalysts [20]. According to this report, the total amount of products formed is approximately three times larger than that found in the absence of O_2. Therefore, it is expected that the radical mechanism will be initiated by oxygen under the present conditions.

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 (condition B) and the results are presented in Table 1 in comparison with those obtained under the condition A. Catalytic properties were improved in all aspects. Although the increase in conversion is marginal, only two products, epoxide and isomerized aldehyde, are observed and the selectivity to campholenic aldehyde is enhanced nearly four times. From these results, it is noticed that the catalyst with hydrophilic nature can be made more active by removing oxygen sources including water and oxygen from the reaction system. In consequence, it is evident that the one-pot procedure for the transformation of α-pinene into campholenic aldehyde was successfully accomplished.

4. Conclusions

Radical-mediated reactions can be suppressed in the conversion of α-pinene by removing water and molecular oxygen simultaneously from the reaction system. This treatment then makes it possible to synthesize campholenic aldehyde in a single step over Ti-HMS catalyst. Therefore, the removal of oxygen sources other than the oxidant is essential for the one-step conversion of α-pinene into campholenic aldehyde.

Acknowledgements

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