Catalysis Communications 59 (2015) 233–237

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Synthesis, characterizations and catalytic allylic oxidation of limonene to carvone of cobalt doped mesoporous silica templated by reed leaves

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ARTICLE INFO

Article history:
Received 17 August 2014
Received in revised form 18 October 2014
Accepted 21 October 2014
Available online 29 October 2014

Keywords:
Cobalt doped mesoporous silica
Allylic oxidation of limonene
Reed leaves
Template
Carvone

ABSTRACT

Reeds (*Phragmites communis*) leaves were successfully used as template in synthesis of cobalt doped mesoporous silica (Co/SiO_2/PC). The catalyst exhibited very high substrate conversion (100%) and relatively good product (carvone) selectivity (40.2%) for allylic oxidation of limonene to carvone using air as oxidant and acetic anhydride as solvent without adding any initiator. Fast hot catalyst filtration experiment proved that the catalyst acted as a heterogeneous one and it can be recycled easily and reused two times without significant loss of activity and selectivity.

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1. Introduction

It is well known that allylic oxidation of cyclic alkenes is of considerable value for the production of unsaturated alcohols and ketones which play a significant role in the development of value-added chemicals from biomass [1,2]. Carvone, one of the most valuable compounds derived from the allylic oxidation of limonene, has wide applications in food additives, fragrance and pharmaceutical industries [3]. The classical methods for the synthesis of carvone from limonene, such as the epoxidation and the nitrosochlorination, are often performed in environmentally unfriendly solvents, producing toxic end-products and difficult to separate products [4]. Compared with these systems, heterogeneous catalysts with more significant advantages for recovery and stabilities are more desirable to liquid-phase oxidation. Recently, a number of solid catalysts were reported for the synthesis of carvone in heterogeneous processes, such as modified silica and titania [5–7]. Chromium containing mesoporous molecular sieves MCM-41 were used to catalyze the allylic oxidation of limonene under mild solvent-free conditions resulting in 36% substrate conversion and 25% selectivity for carvone [5]. A high conversion of 97% of limonene was attained in the presence of V_2O_5/TiO_2 as catalyst but with the corresponding selectivity of only 5.1% towards carvone [6]. With limonene over Mn(Salen) complexes grafted on functionalized SBA-15, it gave the maximum conversion 75.9% whereas the maximum selectivity of carvone is only 7.2% [7]. Moreover, this reaction has been carried out employing metal complexes (manganese [8], cobalt [9] and iron [10]) and MOFs (metal organic frameworks) as catalysts but associated with problems of their hydrothermal and chemical stability compared to that of oxides [11]. Biotransformation was also introduced to synthesize carvone from limonene, which are promising for their green credentials and their high level of sustainability but the yield of carvone is still low [12]. Therefore, from both an economic and environmental point of view, it continues to be a challenge to develop "green" catalysts for the production of carvone, which are active under mild conditions, and which can be easily recovered and reused.

Mesoporous silica has a potential for applications in field of catalysis, sorption and separation due to their ordered pore arrangement, high surface area and relatively high thermal stability [13,14]. And the incorporation of cobalt into mesoporous silica framework and the resulting excellent catalytic activity had been widely investigated [15,16].

Biotemplating techniques have attracted considerable attention for the syntheses of porous inorganic materials in the recent several years, because biological templates are generally energy-conserving, green, and can be harvested in large amounts at low costs. In addition, the method is generally performed under mild conditions, energy-conserving and has little requirement for instrumentation [17–20]. The advantage of biotemplating processes is that they not only yield advanced synthetic materials in an environment benign system but also enable control over the phase, size, morphology achieved by replication or morphosynthesis of biological tissues and materials [21,22]. However, the application of these biotemplated materials in selective oxidation was still very limited. For example, a biological template (*Luffa sponge*) was used as macroscale sacrificial structure builder to synthesize MFI-type zeolite frameworks with hierarchical porosity and complex architecture [23]. Interestingly,

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http://dx.doi.org/10.1016/j.catcom.2014.10.022
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the as-synthesized biomimetic ZSM-5 replica showed catalytic activity for cracking of n-hexane with no need for ion-exchange [24]. In our group cobalt doped porous titania–silica was synthesized by using rice husks as both silicon source and template. It presented good product (4-pyridinecarboxylic acid) selectivity (91%) and very high substrate conversion rate (96%) for the catalytic oxidation of 4-methyl pyridine [25]. Recently, we used natural rubber latex as template in synthesis of cobalt doped mesoporous alumina which was an efficient catalyst for the oxidation of the tetralin under relatively mild reaction conditions. It even offered significantly higher activity than same alumina prepared by conventional templates such as poly (ethylene oxide)-block-poly (propylene oxide)-block-poly (ethylene oxide) (P123) [20].

Reed (*Phragmites communis*) is a widespread perennial plant that grows in wetlands or near inland waterways. Due to the presence of nanocavities and channels, the reed leaves possess hierarchical pore network and complex functional patterns, an excellent gas and water permeability for substrates and products to be diffused in and out, as well as biogenic doped chemical elements, which might be particularly suitable for catalysis and separation [26,27]. Herein, in the continuation of our work, cobalt doped hierarchical mesoporous SiO_2 was synthesized by using reed leaves as the template (denoted as $Co/SiO_2/PC$) and displayed good catalytic properties for the allylic oxidation of limonene to carvone. Additionally, molecular oxygen to oxidation reactions offers a green alternative to traditional toxic chemical oxidants [13]. In our work, atmospheric air was employed as oxidant which is more readily available and could further reduce the cost and hazards of the oxidation process.

2. Experimental

Experimental details for the synthesis of catalysts, oxidation of limonene and characterizations were described in detail in Supplementary data.

3. Results and discussion

3.1. The characterization of catalyst

The N_2 adsorption/desorption isotherm of $Co/SiO_2/PC$ at 77 K is shown in Fig. S1. The sample showed typical isotherm of type IV having inflection around $P/P_0 = 0.4$–0.9. This is typical of mesoporous structure of prepared material and also supported by the big average pore diameter of 4.6 nm, a BET surface area of 435 m^2/g and a pore volume of 0.52 cm^3/g. Moreover, the BJH pore size distribution of $Co/SiO_2/PC$ (inset of Fig. S1) shows one primary pore size distribution in the mesoporous region between 2.1 and 5.6 nm which reveals that the prepared catalyst has irregular pore channels [24,28].

Fig. S2 presents the wide and low (inset) angle X-ray diffraction (XRD) pattern of $Co/SiO_2/PC$ measured at 2θ of 10–80°. Obviously, the structure of silica present in our sample remained essentially amorphous and no distinct diffractions corresponding to any crystalline cobalt are observed. This implies that cobalt species are well incorporated into the silica framework [29]. Similar observations have been reported for Co/MCM-41 and Co/SBA-3 [24]. In addition, it is seen that the low angle XRD pattern of the sample at 2θ of 0–6° shows several diffraction lines in distinct peak in the low 2θ of region. It is clearly indicated that the sample possesses a mesoporous structure [30], which is in agreement with the result of N_2 adsorption/desorption measurement.

To further confirm the valence state of Co species in the resulting sample, an XPS experiment was used for the surface analysis of $Co/SiO_2/PC$. As shown in Fig. S3, the binding energies of doublet for 2p3/2 and 2p1/2 of Co^{2+} are 781.4 and 796.9 eV, respectively. It is also shown that the state of Co species in $Co/SiO_2/PC$ catalyst is the same as that in Co/MCM-41.

Scanning electron microscopy (SEM) images given in Fig. 1 show the morphologies of $Co/SiO_2/PC$ and their template. It is obvious that the microstructure of $Co/SiO_2/PC$ with pore system is well-distributed and compact, which elaborately duplicated the original hierarchical structure such as the sophisticated vascular bundle and stomata of the reed leaves template. The morphology of the honeycomb-like pores and vessels, including cylindrical and also some irregular shapes with random size at 10–20 μm, was obtained.

3.2. Catalytic performance

The catalytic activities of different catalysts for the oxidation of limonene were summarized in Table 1. It is apparent that $Co/SiO_2/PC$ shows the highest conversion and selectivity of carvone. As expected, pristine SiO_2/PC and MCM-41 showed much lower conversion and selectivity than $Co/SiO_2/PC$. This indicates that Co ions in $Co/SiO_2/PC$ are active species for the allylic oxidation of limonene. Furthermore, even incorporating Co into other mesoporous materials, such as Co/MCM-41 and Co/SBA-15 with similar concentrations of cobalt, we found that they exhibited much lower activity than $Co/SiO_2/PC$ though Co/MCM-41 and Co/SBA-15 have much bigger surface area (BET surface areas: 945 m^2/g and 690 m^2/g, respectively) than $Co/SiO_2/PC$. This could be attributed to the pore diameter of $Co/SiO_2/PC$ (4.6 nm) which is larger than Co/MCM-41(2.9 nm) and Co/SBA-15 (3.2 nm) since the catalytic transformation of limonene to products requires suitable catalysts with pores large enough to avoid steric hindrance [31]. To study the catalytic activity of materials with large pore diameter, we chose the SBA-3 as the catalyst support. The pore diameter of cobalt doped SBA-3 (4.5 nm) was smaller in comparison with pure SBA-3 (5.4 nm), but close to that of $Co/SiO_2/PC$ (4.6 nm). However, we found that Co/SBA-3 showed much lower activity than $Co/SiO_2/PC$ although Co/SBA-3 has much larger surface area (780 m^2/g) and similar pore diameter to the $Co/SiO_2/PC$. Therefore, it is suggested that not only pore diameter but also pore structure and morphology of catalyst would play an important role in catalytic oxidation of limonene.

The diffusion of molecules through the pore structure, called "molecular traffic control", is vital for catalytic performance. $Co/SiO_2/PC$ possess heterogeneous pores and complex architecture including honeycomb-like, cylindrical and some irregular shapes, which could help guest species to overcome the intra-diffusional resistance in host materials and allow a rapid diffusion of bulky products through the inorganic networks of pores and channels to ensure high selectivity of catalytically active sites and to avoid over-oxidation [17,18,24]. Thus, due to the good performance of $Co/SiO_2/PC$, in the following we concentrate on the study of the influence of various parameters on the limonene conversion and selectivity of carvone over $Co/SiO_2/PC$.

3.3. Effect of solvents

The nature of solvents was known to have a major influence on reaction kinetics and product conversion in the oxidation of limonene. Therefore, the effects of various solvents on the reaction are investigated and summarized in Table S1. Apparently, using acetic anhydride as the solvent indicated the best catalytic performance. This is probably because polar solvents acetic anhydride may facilitate formation of active oxygen species and thereby enhance allylic oxidation involved free radicals [32].

3.4. Effect of reaction temperature

The effect of reaction temperature on limonene reactions over $Co/SiO_2/PC$ is shown in Fig. 2. It is clear that both conversion of limonene and selectivity of carvone increased with the increase in reaction temperature and both values passed through a maximum at 348 K. A further increase in the reaction temperature resulted in little change of conversion of limonene but a fast decrease in the selectivity. This would be due to the deep/over oxidation and ring-opening reaction

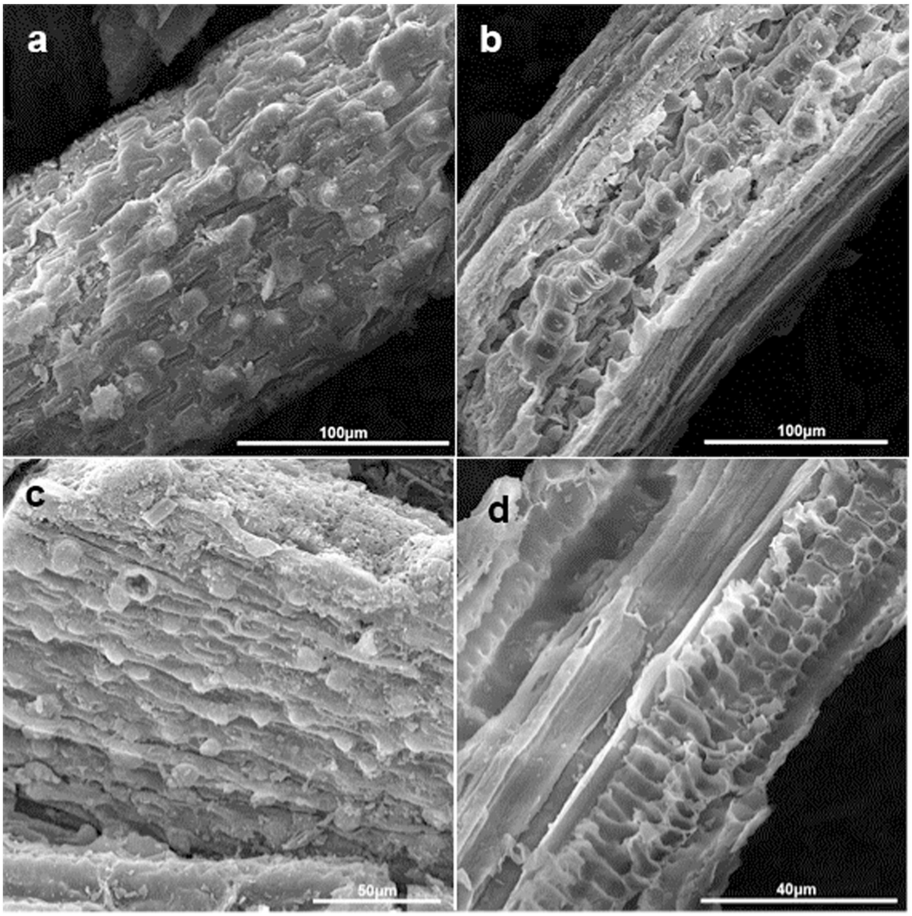


Fig. 1. SEM micrographs of Co/SiO_2/PC and their template. (a, c) Co/SiO_2 synthesized with reed leaf as template and the template tissues after calcination (b) leaf vascular, (d) leaf stomata.

that occurred with the rising temperature when limonene was almost completely converted after 348 K. Because the oxidation of limonene involves radical intermediates and a competition between allylic oxidation and epoxidation. The co-products was also detected to be limonene glycol, carveyl acetate, diepoxide, perillaldehyde and 1,2-diacetoxy-p-mentha-8-ene. Considering the effect of temperature on both conversion of limonene and selectivity of carvone, we chose 348 K as the suitable temperature for the oxidation of limonene.

3.5. Effect of reaction time

The effect of reaction time on limonene reaction over Co/SiO_2/PC was investigated in Fig. 3. A steep increase in the conversion of limonene and selectivity of carvone were observed when the time was increased up to 18 h. Beyond this time, the selectivity of carvone decreased with increase in reaction time. Considering the effect of time on both conversion of limonene and selectivity of carvone, the optimum yield of carvone could be achieved at about 18 h.

3.6. Effect of catalyst concentration

Fig. 4 presents the effect of catalyst concentration on the reaction over Co/SiO_2/PC. It is seen that an initial steep increase in the conversion

Table 1
Comparison of catalytic activities of different catalysts for the oxidation of limonene. [a]

Catalyst	Conversion of limonene (wt.%)	Selectivity of carvone (wt.%)	TON
Co/SiO_2/PC	100	40.2	632
SiO_2/PC	35.7	22.5	–
Co/MCM-41	47.5	34.6	300
MCM-41	16.7	12.8	–
Co/SBA-15	50.2	21.7	317
Co/SBA-3	65.1	18.5	411

[a] Note: Reaction condition: substrate, 2 mL limonene; reaction time, 18 h; reaction temperature, 348 K; catalyst, 100 mg; solvent, acetic anhydride 12 mL; oxidant, air. TON, turn over number (millimole of oxidized products per millimole of metal in the catalyst).

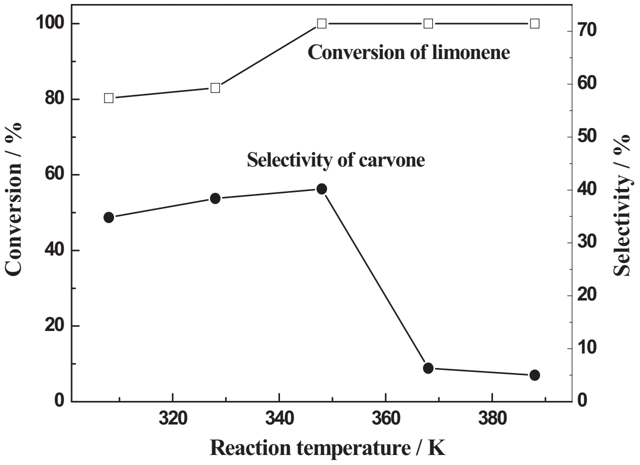


Fig. 2. Effect of temperature on the oxidation of limonene over Co/SiO_2/PC. (Reaction condition: substrate, 2 mL limonene; reaction time, 18 h; catalyst, 100 mg; solvent, acetic anhydride 12 mL; oxidant, air.)

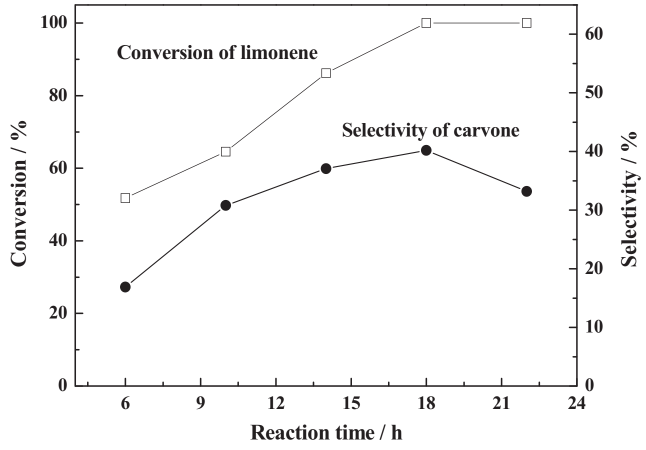


Fig. 3. Effect of reaction time on the oxidation of limonene over Co/SiO_2/PC. (Reaction condition: substrate, 2 mL limonene; reaction temperature, 348 K; catalyst, 100 mg; solvent, acetic anhydride 12 mL; oxidant, air.)

of limonene and a slight increase in selectivity of carvone were observed when the amount of the catalyst was increased up to 100 mg. Beyond this amount, both of the conversion and the selectivity decreased. Thus only small amount of catalyst was active in the oxidation of limonene. This could be attributed to the competent interaction of metal oxo-species in Co/SiO_2/PC matrix with limonene [33], thus inhibiting the catalytic reaction. And it is also probable that large catalyst dosages provide excess active sites in the system to accelerate side reactions. Therefore, 100 mg was selected as the suitable amount of the catalyst for oxidizing limonene.

3.7. Oxidation of limonene with different molar ratio of Si/Co

Meanwhile, the influence of the Si/Co on the catalytic activity is shown in Table S2. It indicates that the suitable ratio of Si/Co is 60. However, the decrease in limonene conversion and carvone selectivity at higher cobalt content (Si/Co of 60) could be due to the presence of excess amount of cobalt, which leads to competent interaction of metal oxo-species with both alkylperoxy species and substrate [24,34].

3.8. The reusability and fast hot catalyst filtration experiment

To study the stability and recycling ability of Co/SiO_2/PC under reaction conditions, recycling experiments were carried out. The reactions were also under the optimum conditions with those used for Co/SiO_2/PC. The typical recycling procedure was as follows: after the initial reaction, the catalyst was separated from the reaction mixture and washed with alcohol and acetone, dried at 363 K, followed by the activation at 773 K for 2 h. The results are also summarized in Table 2; the catalyst Co/SiO_2/PC showed excellent reusability in the oxidation reactions. Moreover, the Co 2p XPS spectra of the fresh Co/SiO_2/PC and the recycled Co/SiO_2/PC (reacted at 348 K for 18 h) were collected to determine the state of the Co active sites (Fig. S3). It was found that their spectra were similar, which indicated that the state of the Co active site in the recycled Co/SiO_2/PC catalyst changed little in the first catalytic activity test when compared with those of fresh Co/SiO_2/PC.

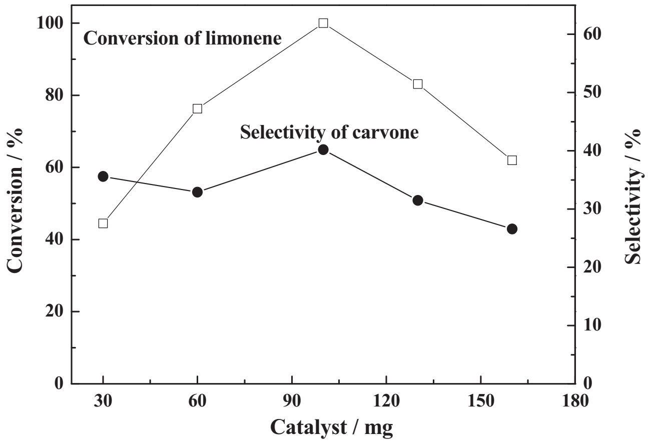


Fig. 4. Effect of catalyst concentration on the oxidation of limonene over Co/SiO_2/PC. (Reaction condition: substrate, 2 mL limonene; reaction temperature, 348 K; reaction time, 18 h; solvent, acetic anhydride 12 mL; oxidant, air.)

In order to prove whether the catalyst is a heterogeneous one, experiments with fast hot catalyst filtration and studying the activity of the filtrate had been done by a modified process as Ref. [34]. We found that after hot filtration the filtrate reacted little further comparing that observed when the catalyst was not filtered. This observation was also well supported by ICP-AES analysis of filtrates where negligible amount of leaching of active cobalt $\leq$0.001%. These indicated that the doped active component (cobalt) did not leach to the solution and the Co/SiO_2/PC did act as a heterogeneous catalyst.

Allylic oxidation and epoxidation are often competitive processes in the oxidation of cyclic olefins and frequently both processes occur simultaneously. Typically, the abstraction of the allylic hydrogen gives allylic oxidation products and the electrophilic attack at to the double bond results in epoxidation or ring cleavage [1]. The limonene liquid phase oxidation may proceed by the pathway/mechanism as illustrated in Scheme 1: (a) epoxidation, leading to limonene-1,2-epoxide or limonene glycol (transformed by ring-opening) as the main product, or (b) allylic oxidation, carvone, and carveol would be the main products though trace amount of some by-products, such as perillaldehyde, p-mentha-1,8-dien-2-ol, p-mentha-2,8-dien-1-ol as well as carveyl acetate were also formed due to the free radical chain reaction mechanism [6,35].

4. Conclusions

In conclusion, reeds (*P. communis*) leaves were successfully used as template in synthesis of cobalt doped mesoporous silica (Co/SiO_2/PC). Co/SiO_2/PC was an efficient and high substrate conversion catalyst for the allylic oxidation of limonene under relatively mild reaction conditions without adding any initiator. It even exhibited significantly higher activity than Co/MCM-41. Fast hot catalyst filtration experiments proved that the catalyst acted as a heterogeneous one; it can be reused three times without losing its activity to any great extent.

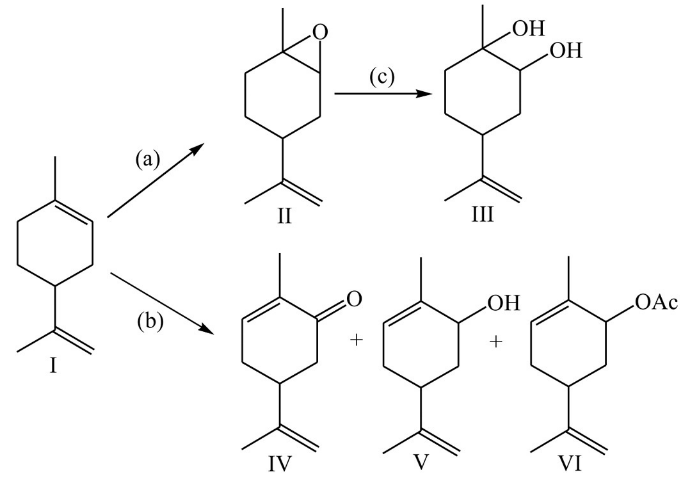
Acknowledgments

The authors thank the National Natural Science Foundation of China (Project NSFC-YN U1033603, 21263027, 21367024), and Program for Innovative Research Team (in Science and Technology) in University of Yunnan Province (IRTSTYN) for financial support.

Table 2
Recycled experiment of catalytic efficiency under optimum condition.[a]

Catalyst	Conversion of limonene (wt.%)	Selectivity of carvone (wt.%)	TON
Fresh	100	40.2	632
First recycled	92.0	43.8	581
Second recycled	90.0	43.0	568

[a] Note: Reaction condition: substrate, 2 mL limonene; reaction time, 18 h; reaction temperature, 348 K; catalyst, 100 mg; solvent, acetic anhydride 12 mL; oxidant, air. TON, turn over number (millimole of oxidized products per millimole of metal in the catalyst).



Scheme 1. Possible reaction pathway/mechanism in the oxidation of limonene: (a) concerted process; (b) free radical process; (c) ring-opening process; (I) limonene; (II) limonene-1,2-epoxide; (III) limonene glycol; (IV) carvone; (V) carveol; (VI) carveyl acetate.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.10.022. These data include MOL files and InChiKeys of the most important compounds described in this article.

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