

Catalytic application of an organo superbase dendron grafted on mesoporous SBA-15 and related palladium complex in the aerobic oxidation of alcohols

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Received: 25 October 2013, Accepted: 22 November 2013, Published: 1 February 2014

Abstract

An efficient synthetic method for successful application of amine dendron on SBA-15 and related Pd (II) complex has been developed by employing aerobic oxidation of alcohols as model reactions. The yields of the products were in the range from 75% to 92%. The catalyst can be readily recovered and reused at least 5 consecutive cycles without significant leaching and loss its catalytic activity.

Keywords: Organosuperbase, SBA-15, palladium complex, oxidation

Introduction

Mesoporous materials have attracted considerable interest as catalysts, catalyst supports, adsorbents, sensors, etc. [1-6]. Ordered mesoporous silicas (OMSs), particularly SBA-15 between other silica materials, have relatively good hydrothermal stability, and possesses hexagonal arrays of uniform pores with high special surface area and large pore volume. The presence of palladium species on mesoporous silicas as heterogeneous catalysts is frequently used in various coupling, hydrogenation and oxidative transformations [7-12]. Mesoporous silica supports have high surface area, thermal and mechanical stability and insolubility in organic and aqueous solvents [13]. These several

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properties can be led to presence and uniform distribution of active metals such as palladium, rhodium, ruthenium, cooper, and etc. on their surfaces that can occurred both doping of metal salts at mentioned pores and grafting of organic functional groups lined with spacers that have maintained metal ions on OMSs [14-16]. The production of high density hybrid materials containing organic functional groups on OMSs is difficult because the distribution of catalytically active sites often becomes heterogeneous. To achieve higher densities of homogeneous organic functional groups, the use of surface patterning and molecular imprinting techniques can circumvent this issue [17,18]. In addition to the mentioned methods, surface functionalized with dendrimers are another choice to obtain high organic group densities [19, 20].

Recently, Alizadeh et al. have reported the immobilization of organo superbase groups on the surfaces of SBA-15 materials [21, 22]. The current investigation is a method for synthesis of organo superbase functionalized on SBA-15 (SBA-15/CCMet), its related palladium complex (SBA-15/CCMet/Pd(II)) and describes the catalytic testing of this material in the aerobic oxidation of alcohols.

Experimental section

General

All chemicals were purchased from Merck except Pluronic123 and metformin hydrochloride which were obtained from Aldrich. All Products were characterized by comparison of their physical data, IR and ^1H NMR and ^{13}C NMR spectra and physical, properties with those reported in the literature. IR spectra of the compounds were obtained on a Perkin Elmer using a KBr disk. The catalyst morphology was examined by TEM.

Preparation of SBA- 15/CCMet/Pd(II)

The synthesis of SBA- 15/CCMet/Pd(II) was performed following our previous report [23].

Catalytic testing

Aerobic oxidation of alcohols

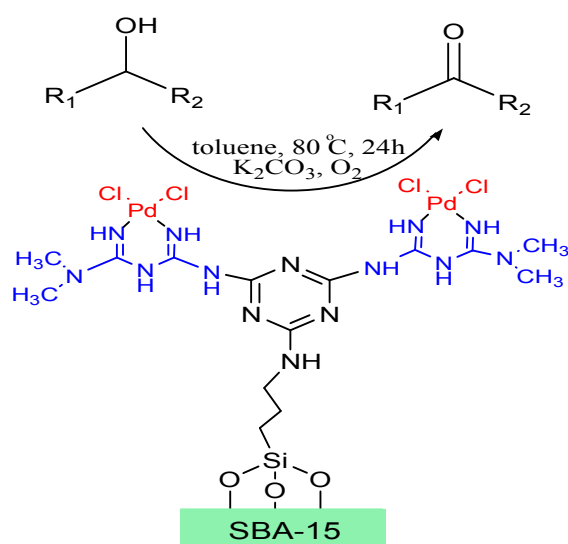
A mixture of K_2CO_3 (1 mmol) and the catalyst (40 mg) in toluene (5 mL) was prepared in a two necked flask. The flask was evacuated and refilled with pure oxygen. The alcohol (1 mmol, in 1 mL toluene) was injected into this solution and the resulting mixture was stirred at 80 °C under an oxygen atmosphere. After completion of reaction, the reaction mixture was filtered off and the catalyst rinsed twice with CH_2Cl_2 (5 mL). The excess of solvent was removed under reduced

pressure to give the corresponding carbonyl compounds.

Results and discussion

The amine-functionalized dendron SBA-15 anchored palladium (II) complex (SBA-15/CCMet/Pd(II)) was conveniently synthesized from commercially available and cheap materials via immobilization on SBA-15 according to our previous publication.²³

In order to evaluate catalytic activity of the prepared hybrid material SBA-15/CCMet/Pd(II) as a heterogeneous catalyst, the aerobic oxidation of alcohols was chosen as probe reaction (Scheme 1).



Scheme 1. Aerobic oxidation of various alcohols catalyzed by SBA-15/Met/Pd(II)

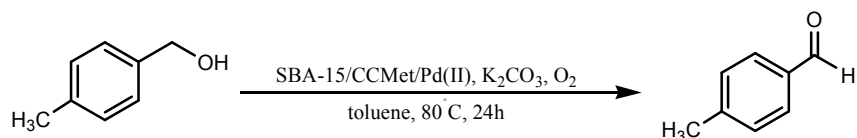
The oxidation of *para*-methylbenzyl alcohol using various amount of the prepared catalyst was performed under O₂ in balloon. In the presence of the heterogeneous catalyst and optimized conditions, *para*-methylbenzaldehyde was obtained in excellent yield. It was important to note that oxidation did not proceed when palladium source (catalyst) was not added. The desired product

was obtained only in 28 % yield when without using an appropriate base, 2.5% mol of catalyst was used at 80 °C and 24 h (Table 1, entries 1-4). Using K₂CO₃ as the appropriate base resulted in 96 % yield of the desired product (Table 1, entry 8).

The scope of the presented catalyst system was then subsequently extended to the aerobic

oxidation of a large variety of alcohols under same conditions. Substituted benzyl alcohols containing electron-donating groups such as CH₃ and OCH₃ (Table 3, entries 2,3) are more easily oxidized than those containing electron-withdrawing groups (Table 2, entry 4). Secondary benzylic alcohols were also converted to the corresponding ketones in quantitative yields (Table 2, entry 5,6,9). A complete conversion of allylic alcohols, for example, cinnamyl alcohol, to the desired aldehydes was achieved within 24 h (Table 2, Entry 7). The C=C double bonds remained intact without an intramolecular hydrogen transfer over SBA-15/Met/Pd(II) under the investigated conditions. Our catalyst was also applicable to the oxidation of various aliphatic alcohols including primary and secondary linear, and cyclic aliphatic alcohols, to afford the corresponding aldehydes or ketones in excellent yields within short reaction times under mild conditions (Table 2, entries 8–11).

Table 1.



Entry	Catalyst amount (%mol)	T(°C)	Base	T (h)	run	Yield (%) ^a
1	1	25	-	24	1	NR
2	1	80	-	24	1	trace
3	2	80	-	24	1	15
4	2.5	80	-	24	1	28
5	2.5	80	K ₂ CO ₃	1	1	54
6	2.5	80	K ₂ CO ₃	5	1	80
7	2.5	80	Et ₃ N	24	1	93
8	2.5	80	K ₂ CO ₃	24	1	96
9	2.5	80	K ₂ CO ₃	24	2	92
10	2.5	80	K ₂ CO ₃	24	3	91
11	2.5	80	K ₂ CO ₃	24	4	89
12	2.5	80	K ₂ CO ₃	24	5	89

^aIsolated yield

Figure 1 shows the reusability of the SBA-15/Met/Pd(II) for aerobic oxidation of *para*-methylbenzyl alcohol in 24 h (Table 2, Entry 3). After the catalytic reaction, the catalyst was isolated from the liquid phase by centrifugation, thoroughly washed with ethanol, and then reutilized as catalyst in subsequent runs under identical reaction conditions. The results included in Figure 1 indicate that no efficiency loss and palladium

leaching was observed in the aerobic oxidation of alcohol for up to five runs.

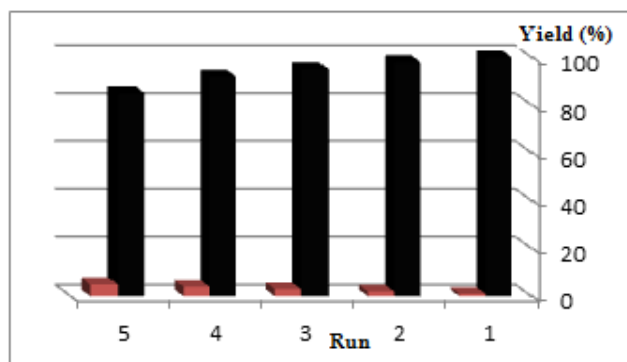
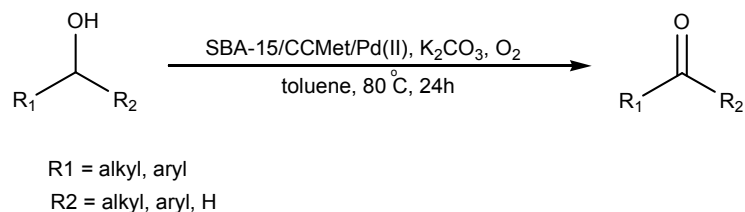
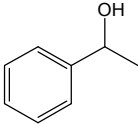
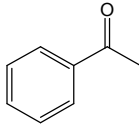
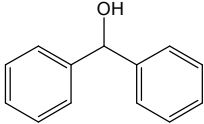
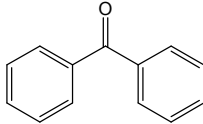
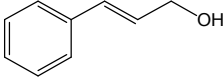
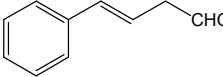
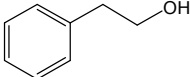
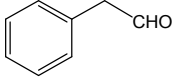
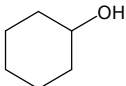
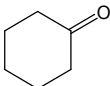
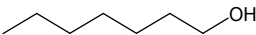
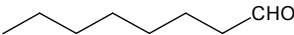
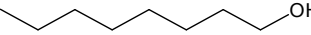
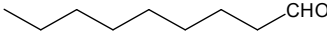


Figure 1. The recycling of the SBA-15/CCMet/Pd(II) for the aerobic oxidation of *para*-methylbenzyl alcohol

Table 2. Aerobic oxidation of various alcohols catalyzed by SBA-15/Met/Pd(II)



Entry	Substrates	Products	Yield (%)
1			98
2			96
3			96
4			90

5			96
6			92
7			92
8			92
9			80
10			90
11			90

Conclusion

In summary, the successful application of the catalyst from commercially available starting materials in the aerobic oxidation of alcohols under feasible conditions is reported. The structural explanations of these materials suggest that they have stable structure with relevant organic components covalently attached to their surfaces. The benefits of this catalyst are cheaper and uncomplicated synthetic pathway, milder and more efficient uses for oxidation reaction in green media, which make them appropriate possibility for

commercial utilization. Notably, the recyclability of the catalyst with no palladium leaching in SBA-15/CCMet/Pd(II) and several times reusing without any decreases in activity are good characteristics.

Acknowledgement

We appreciate Payame Noor University for their partial support on this project.

References

- [1] A. Anan, K.K. Sharma, T. Asefa, *J. Mol. Catal. A: Chem.*, **2008**, 288, 1-13.

- [2] Z. Zhou, Q. Meng, A. Seifert, A. Wagener, Y. Sun, S. Ernst, W.R. Thiel, *Micropor. Mesopor. Mat.*, **2009**, *121*, 145-151.
- [3] Q. Meng, X. Zhang, C. He, P. Zhou, W. Su, C. Duan, *Talanta*, **2011**, *84*, 53-59.
- [4] S. Somacescu, P. Osiceanu, J.M. Calderon Moreno, L. Navarrete, J.M. Serra, *Micropor. Mesopor. Mat.*, **2013**, *179*, 78-88.
- [5] S. Tao, Z. Zhu, C. Meng, C. Wang, *Micropor. Mesopor. Mat.*, **2013**, *171*, 94-102.
- [6] M. Mazloum-Ardakani, M.A. Sheikh-Mohseni, M. Abdollahi-Alibeik, A. Benvidi, *Sensor. Act. B: Chem.*, **2012**, *171-172*, 380-386.
- [7] K. Dhahagani, J. Rajesh, R. Kannan, G. Rajagopal, *Tetrahedron: Asymmetry*, **2011**, *22*, 857-865.
- [8] M. Ghashghaee, R. Karimzadeh, *Micropor. Mesopor. Mat.*, **2013**, *170*, 318-330.
- [9] S.L. Hruby, B.H. Shanks, *J. Catal.*, **2009**, *263*, 181-188.
- [10] M.N. Parvin, H. Jin, M.B. Ansari, S.-M. Oh, S.-E. Park, *Appl. Catal. A: Gen.*, **2012**, *413-414*, 205-212.
- [11] Q. Wang, V.V. Guerrero, A. Ghosh, S. Yeu, J.D. Lunn, D.F. Shantz, *J. Catal.*, **2010**, *269*, 15-25.
- [12] T. Yokoi, Y. Kubota, T. Tatsumi, *Appl. Catal. A: Gen.*, **2012**, *421-422*, 14-37.
- [13] Y. Shao, J. Guan, S. Wu, H. Liu, B. Liu, Q. Kan, *Micropor. Mesopor. Mat.*, **2010**, *128*, 120-125.
- [14] J. Demel, J. Čejka, P. Štěpnička, *J. Mol. Catal. A: Chem.*, **2010**, *329*, 13-20.
- [15] M.-J. Jin, A. Taher, H.-J. Kang, M. Choi, R. Ryoo, *Green Chem.*, **2009**, *11*, 309-313.
- [16] W. Chen, P. Li, L. Wang, *Tetrahedron*, **2011**, *67*, 318-325.
- [17] J.C. Hicks, R. Dabestani, A.C. Buchanan, C.W. Jones, *Chem. Mat.*, **2006**, *18*, 5022-5032.
- [18] H. Li, J. Lü, Z. Zheng, R. Cao, *J. Colloid Inter. Sci.*, **2011**, *353*, 149-155.
- [19] M. Bhagiyalakshmi, S.D. Park, W.S. Cha, H.T. Jang, *Appl. Sur. Sci.*, **2010**, *256*, 6660-6666.
- [20] A. Shahbazi, H. Younesi, A. Badiie, *Chem. Eng. J.*, **2011**, *168*, 505-518.
- [21] A. Alizadeh, M.M. Khodaei, D. Kordestani, A.H. Fallah, M. Beygzadeh, *Micropor. Mesopor. Mat.*, **2012**, *159*, 9-16.
- [22] A. Alizadeh, M.M. Khodaei, D. Kordestania, M. Beygzadeh, *J. Mol. Catal. A: Chem.*, **2013**, *372*, 167-174.
- [23] H. Veisi, D. Kordestani, A.R. Faraji *J. Porous Mater.*, **2013**, doi:10.1007/s10934-013-9758-3.