Catalysis Letters, Vol. 114, Nos. 3–4, April 2007 (© 2007)
DOI: 10.1007/s10562-007-9061-5

An efficient oxidation of toluene over Co(II)TPP supported on chitosan using air

Guan Huang,* Ai P. Wang, Shang Y. Liu, Yong A. Guo, Hong Zhou, and Shu K. Zhao

College of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

Received 10 January 2007; accepted 1 February 2007

An efficient oxidation of toluene to benzaldehyde and benzyl alcohol is accomplished over chitosan(CTS)-supported Co(II)TPP catalyst [Co(II)TPP/CTS] under a relatively mild reaction condition using air in absence of reductants and solvents, it can be reused for five times, with average selectivity of 65%, average toluene conversion of 8.83% and average turnover number of 69804.

KEY WORDS: chitosan; cobalt tetraphenylporphyrin; toluene oxidation; air.

1. Introduction

Toluene can be oxidized into benzaldehyde, benzyl alcohol and benzoic acid, which are versatile intermediates in the chemical industry [1]. Although the gas phase partial oxidation of some alkylaromatics has gotten ahead, the vapour phase selective oxidation of toluene with high yields of the valuable intermediate products is still a challenge, the liquid phase route being industrially preferred [2, 3]. The increased environment concerns in recent years call for benign oxidants such as molecular oxygen or hydrogen peroxide [4]. But the present oxidation of toluene with air could not produce benzaldehyde and benzyl alcohol because it was difficult to effectively prevent the over-oxidation of benzaldehyde into benzoic acid during the oxidation of toluene [5]. Although the main route of obtaining these compounds is the liquid phase oxidation of toluene, there still exist unavoidable drawbacks in this process, such as undesired products formation, high cost on the successive separation operations, the corrosion problems, the serious pollution, etc.[6]. The present synthetic method of benzaldehyde and benzyl alcohol by the chlorination of toluene followed by hydrolysis (used in the world industry) [7] and by the oxidation of toluene over the vanadium-containing catalysts [8] obtained the best selectivity of benzaldehyde and benzalcohol, but which do not exceed 40–60%. A new method of selective oxidation of toluene with clean oxidants to benzaldehyde and benzyl alcohol has been an attractive field.

Metalloporphyrins are known for high activity for the catalytic oxidation of the inert carbon-hydrogen bond in hydrocarbon under mild conditions [9]. However, the catalysts in homogeneous system are inclined to an easy deactivation and are difficult to be recovered from the reaction mixtures, leading to many restrictions in large-scale process. Besides, metalloporphyrins are often expensive to purchase, synthesize and manipulate. Therefore, much effort have devoted on development of solid supports to immobilization of metalloporphyrins [10]. Up to now there are few reports about the directive oxidation of toluene with air catalyzed by supported metalloporphyrins. The reason possibly is that vanadium-containing catalysts are more attractive for some chemists [11]. Herein, we report an efficient oxidation of toluene repeatedly over Co(II)TPP/CTS in environmentally benign reaction condition using air in absence of reductants and solvents.

2. Experimental

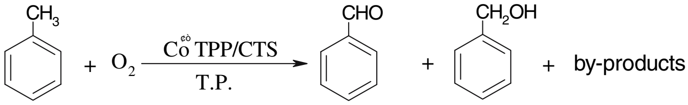
All reagents and solvents used were of analytical grade and were obtained commercially. Co(II)TPP was synthesized according to published procedures [12, 13]. No impurities were found in the toluene by GC analysis before use.

UV-Vis spectra were recorded on a Perkin-Elmer L-17 spectrometer. GC analysis of catalytic oxidation products was accomplished using a Shimadzu GC-16A chromatograph equipped with a 0.5 mm i.d. × 25 m PEG20000 capillary column and flame ionization detector. The reactor was a model KCF-10 500 ml autoclave fitted with a magnetic stirrer and a model CYS-1 digital oxygen meter.

Co(II)TPP/CTS catalyst with a Co(II)TPP/ CTS ratio of 0.0435 mmol/g was prepared according to a

---

*To whom correspondence should be addressed.
E-mail: huangg66@126.com



Scheme 1.

procedure similarly described elsewhere [14] and was characterized by UV-Vis spectroscopy, using the similar method [15]. The electronic spectra of the supported catalyst was obtained in glycerol mull in quartz vessel and compared with that of Co(II)TPP in the region of 300–550 nm (figure 1). The chloroform extraction from the powder of the solid catalyst was measured using UV-Vis spectrometer, with the results shown in (figure 1a).

The toluene oxidation catalyzed by Co(II)TPP/CTS with air was as follows (Scheme 1):

The main oxidation products were benzaldehyde and benzyl alcohol, with the by-products, benzoic acid and benzyl benzoate, as confirmed by GC-MS analysis.

In a typical reaction procedure, toluene (350 ml) was mixed with Co(II)TPP/CTS catalyst (containing 5 mg cobalt porphyrin) in a 500 ml autoclave reactor and heated to 433 K under vigorous stirring in an air pressure of 0.8 MPa. The reaction mixture was sampled out at regular intervals and analyzed by GC-MS. Quantification of the oxygenated products was obtained by GC using chlorobenzene as the internal standard [16]. The supported catalyst was recovered by simple separation from the reaction mixture followed by washing with alcohol and drying in air, and it was used in subsequent toluene oxidation.

3. Results and discussion

Co(II)TPP was successfully supported on CTS as shown by the UV-Vis spectra of a suspension of the material in glycerol mull. The spectra present the characteristic Soret band of the metalloporphyrin at 417 nm and the Q band at 524 nm, as shown in figure 1b.The presence of the unchanged Soret bands and the Q band indicates that the Co(II)TPP was immobilized on the structure of the support. The chloroform extraction from the powder of the solid catalyst presented the same bands as those shown in figure 1a, again indicating that the metalloporphyrin has been adsorbed on the support.

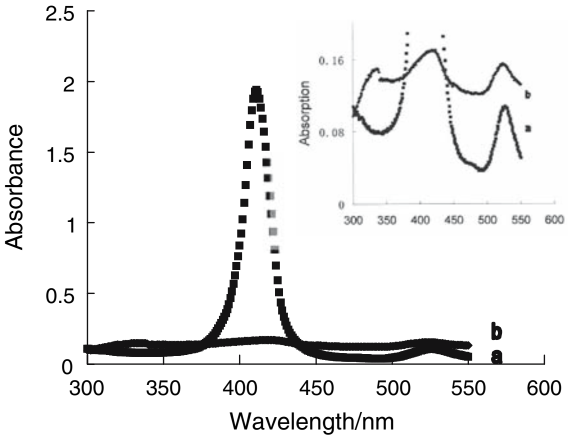


Figure 1. UV-Vis spectra at room temperature: (a) chloroform solution of Co(II)TPP, (b) in glycerol mull Co(II)TPP on chitosan.

The results of aerobic oxidation of toluene over the supported catalyst in absence of coreductants and solvents have been compared with those over the unsupported cobalt porphyrin catalyst at the same reaction condition (Table 1). A more efficient oxidation of toluene to aldehyde and alcohol could be accomplished at 433 K and 0.8 MPa air pressure using Co(II)TPP/CTS as catalyst (Table 1, entries 1–5). Turnover number (TON) as high as approximately 70000 could be achieved which is better than many of the catalyst systems reported earlier. The conversion in the toluene oxidation was almost the same as that by cobalt porphyrin. These indicate that the supported catalyst keeps the same strong power of converting toluene to the products as Co(II)TPP, but has a slightly high proportion of benzaldehyde and benzyl alcohol, just as Table 1 shows.

In general, the increasing rates of the amounts of the desired products (aldehyde and alcohol) with reaction time are greater than that for any by-product, such as benzoic acid or benzoic ester (too little amount, be omitted herein) under the catalysis of the supported or unsupported catalyst. However, the increasing rate of the amount of benzoic acid with reaction time for Co(II)TPP is always greater than that for Co(II)TPP/CTS (see figure 2). Obviously, the yields of the main

Table 1

Results of aerobic oxidation of toluene catalyzed by different catalysts

Catalyst	Oxidation cycle	Selectivity (mol%)			Conversion (mol%)	Turnover numbers
		Aldehyde	Alcohol	Acid		
Co(II)TPP		33	26	40	8.07	63720
Co(II)TPP/CTS	1	37	29	33	8.93	70510
	2	36	28	35	8.86	69947
	3	38	27	33	8.89	70237
	4	35	30	34	8.53	67818
	5	37	28	34	8.93	70510
	average	37	28	34	8.83	69804

Reaction time: 4.5 h.

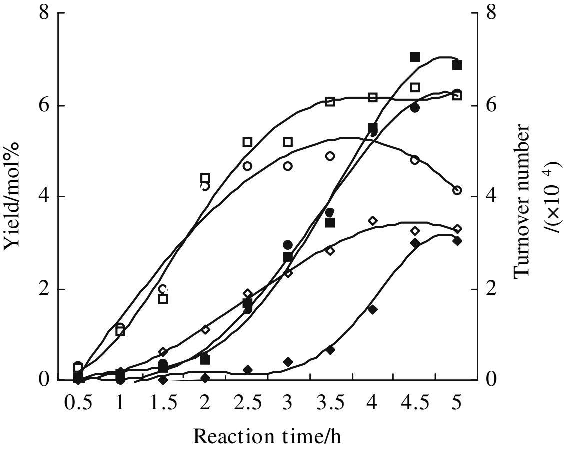


Figure 2. Changes in mole percent of reaction products and in turnover number with reacti on time for toluene oxidation catalyzed by Co (II) TPP and Co (II) TPP/CTS, respectively (○- and ●-benzaldehyde + benzyl alcohol, ◇- and ◆-benzoic acid; □- and ■-turnover number).

products and the catalyst TON have been improved in toluene oxidation catalyzed by the supported catalyst with the assistant catalysis provided by chitosan.

It means that the selectivity for aldehyde and alcohol in the toluene oxidation catalyzed by the heterogeneously catalytic system is little better than that for the homogeneous in our reaction system. The excellent selectivity in the toluene oxidation catalyzed by the supported catalyst can be seen from figure 3. Although the selectivity for benzaldehyde and benzyl alcohol in the oxidation catalyzed by either Co (II) TPP/CTS or Co (II)TPP with reaction time are all decreased, the former catalyst has slightly different selectivity from the latter throughout the aerobic oxidation of toluene. This selective discrepancy for the supported catalyst probably comes from its particular catalysis, which has a shorter time of conversion toluene into the desired products with the highest concentration and then a decrease of over-oxidation of aldehyde and alcohol to by-products, such as, benzoic acid. There was an induction period about 2 h for the supported catalyst used in toluene oxidation. After being activated, it only cost 2.5 h to reach the maximum of toluene conversion (the time calculated from reaction time 2–4.5 h). The period of time is very important for it because the toluene and the desired products were quickly oxidized into products and by-products, respectively (see figures 2 and 3). Cobalt porphyrin, however, needed 3.5 h (from 0.5 to 4 h) for arrival of the corresponding toluene conversion, and it has no induction period. The more the desired products and the longer they stay in reaction system for, the more the by-product (benzoic acid) and the lower the selectivity for the aldehyde and alcohol (see figure2, 3 and Table 1). The results above illuminate that there are different catalysis for toluene oxidation between the two catalysts.

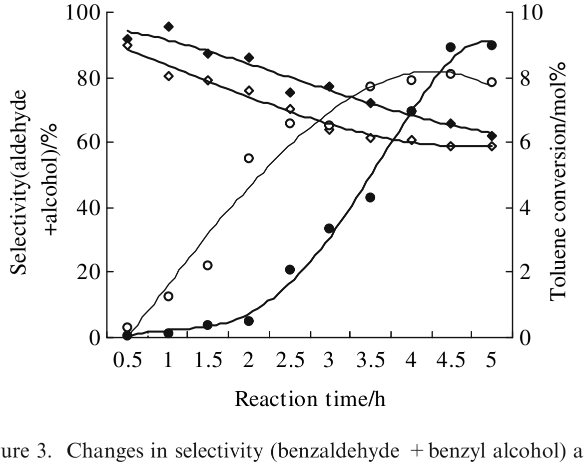


Figure 3. Changes in selectivity (benzaldehyde + benzyl alcohol) and conversion with reaction time for toluene oxidation catalyzed by Co (II) TPP and Co (II) TPP/CTS (◇- and ◆-selectivity; ○- and ●-conversion), respectively.

In the toluene oxidation stages from 0.5 to 2 h, the catalysis of the unsupported catalyst shows that the higher the toluene conversion, the lower the selectivity of the main products. However the change trends are slower for the supported catalyst (see figure3). This relies on the catalytic characteristic of Co(II)TPP/CTS, of which the microenvironment of CTS played an important role [17].

Co(II)TPP supported on CTS was easily to be recovered. Moreover CTS not only protected cobalt porphyrin from the oxidation destruction by oxygen but also provided the nitrogenous microenvironment for Co(II)TPP. The special location more easily afforded the readiness of Co(II)TPP both to bind O_2 to form the high value reactive intermediate [18] and to decompose the peroxide to avoid the over-oxidation of the main products to by-products[19], such as benzoic acid etc. Hence, Co(II)TPP/CTS could perform the efficient oxidation of toluene to benzaldehyde and benzyl alcohol, and could be reused for five times, with average selectivity of 65%, average toluene conversion of 8.83% and average turnover number of 69804.

4. Conclusion

In summary, the supported catalyst, Co(II)TPP/CTS, is a very efficient catalyst for the oxidation of toluene using air in absence of coreductants and solvents. It can be recycled several times for the catalysis and easily recovered by simple isolation from the reaction mixture, more fitting to the practical use in industry than Co(II)TPP. The catalysis for toluene oxidation is related to the nature of interactions between the solid support and metallic complexes. The Co(II)TPP catalysis assisted by the chitosan microenvironment for toluene oxidation is not understood well and further experimental investigations are proceeding.

Acknowledgments

We are grateful for the foundation support of doctoral startup fund and of experimental innovation project fund of Guangxi University, P. R. China.

References

[1] R.A. Sheldon, Chemtech (1991) 556.
[2] B. Grzybowska-Swierkosz, Appl. Catal. 157 (1997) 263.
[3] A. Martin and B. Lucke, Catal. Today 57 (2000) 61.
[4] W. Partenheimer, Catal. Today 23 (1995) 69.
[5] C.C. Guo, Q. Liu, X.T. Wang and H.Y. Hu, Appl. Catal. A Gen. 282 (2005) 55.
[6] H. Gao, G.W. Chen, Q. Yuan and H.Q. Li, Catal. Today 110 (2005) 171.
[7] W. Partenheimer, Catal. Today 23 (1995) 69.
[8] A. Bruckner, Appl. Catal. A Gen. 200 (2000) 287.
[9] J.T. Groves and D.V. Subbramanian, J. Am. Chem. Soc. 106 (1984) 2177.
[10] C. Crestini, A. Pastorini and P. Tagliatesta, J. Mol. Catal. A Chem. 208 (2004) 195.
[11] A. Bottino, G. Capannelli, A. Comite and R.D. Felice, Catal. Today 99 (2005) 171.
[12] A.D. Alder, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour and L.J. Korsakoff, J. Org. Chem. 32 (1967) 476.
[13] A.D. Alder, F.R. Longo, F. Kampas and J. Kim, J. Inorg. Nucl. Chem. 32 (1970) 2443.
[14] C.C. Guo, G. Huang, X.B. Zhang and D.C. Guo, Appl. Catal. A Gen. 247 (2003) 261.
[15] J. Haber, L. Matachowski and K. Pamin, Catal. Today 91 (2004) 195.
[16] C.C. Guo, S.J. Zhu and M.D. Gui, Acta. Chim. Sin. 50 (1992) 129.
[17] G. Huang, C.C. Guo and Si.Si. Tang, J. Mol. Catal. A Chem. 261 (2006) 125.
[18] J. Haber and T. Mlodnicka, J. Mol. Catal. 74 (1992) 131.
[19] X.Y. Wang, R. Wang, G.Q. Li and G.N. Li, Acta Chim.Sin. 45 (1987) 780.