Asian Journal of Chemistry; Vol. 24, No. 9 (2012), 4044-4046

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Kinetic Investigation on Catalysis of Metal-Organic Framework-Type Catalyst with Nano-Sized Channels†

YUN WU[1,*], BEN-HONG YANG[1], MENG LI[1], CHANG-AN TIAN[1] and LING-GUANG QIU[2,*]

[1]Department of Chemical and Materials Engineering, Hefei University, Hefei 230022, P.R. China
[2]School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, P.R. China

*Corresponding author: E-mail: cloudless@hfuu.edu.cn; lgqiu@ahu.edu.cn

AJC-11310

Kinetics of oxidation of benzyl alcohol catalyzed by metal-organic frameworks (MOFs) with nano-sized channels was studied using a simple UV-VIS spectral method by choosing hydrogen peroxide as an oxidant. The effects of molar ratio of the catalyst to the substrate and the reaction temperature on the oxidation of benzyl alcohol to benzaldehyde have been investigated.

Key Words: Kinetics, Metal-organic frameworks, Catalytic oxidation, Benzyl alcohol.

INTRODUCTION

Recently, metal-organic framework (MOF) compounds, which consist of metal oxide/nitride clusters connected by organic linkers, have attracted considerable attention, due to the possibility to control the topology geometry and composition of the infinite framework, as well as their divergent applications in potential catalysis, ion exchange, gas adsorption/separation and catalysis, sensor technologies, magnetization, luminescence, proton conduction and semiconduction[1-6]. In previous work, we have developed a novel kind of hierarchically micro- and mesoporous Cu-based metal-organic framework $[(Cu_3(BTC)_2(H_2O)_3]_n$ with a mesopore system (Ø 3.8 nm) and a micropore system (Ø 0.8 nm) (Fig. 1)[7]. In this work, we mainly describe catalytic oxidation of benzyl alcohol by using such Cu-based metal-organic framework $[(Cu_3(BTC)_2(H_2O)_3]_n$ as a heterogeneous catalyst. In order to have a comprehensive understanding of the selectivity and activity of the catalyst, various factors influencing the catalytical properties of the metal-organic framework, such as molar ratio and temperature were discussed.

EXPERIMENTAL

The metal-organic framework $[(Cu_3(BTC)_2(H_2O)_3]_n$ sample was prepared as described previously[7]. Tri-(hydroxymethyl)aminomethane (Tris), alcohol, acetonitrile, were all of analytical grade and purchased from Sinopharments. All the chemicals and solvents were used as received without further purification. Water used for all kinetic measure was redistilled water. Kinetic investigations were carried out by using UV-VIS spectrophotometer on a Shimadzu UV-3600 double-beam scanning spectrophotometer.

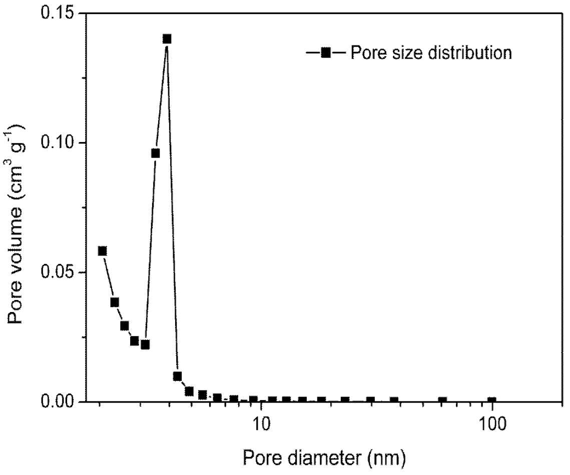

Fig. 1. Pore size distribution for mesoporous $[Cu_3(BTC)_2(H_2O)_3]_n$

RESULTS AND DISCUSSION

Kinetic of reaction selectivity method: Oxidation of benzyl alcohol to benzaldehyde catalyzed by $[(Cu_3(BTC)_2(H_2O)_3]_n$ was investigated by using hydrogen peroxide as an oxidant.

---

†Presented to The 5th Korea-China International Conference on Multi-Functional Materials and Application.

From a typical UV-VIS spectrum, it can be seen a successive increase in the absorption maximum of benzaldehyde at 274 nm. As a result, the absorbance A_t was recorded by monitoring the appearance of benzaldehyde at 274 nm *versus* the reaction time t. The results revealed that the reaction was of the apparent first order with respect to the benzyl alcohol concentration. After the nonlinear fitting of the experimental data, a series of the apparent first-order rate constants for oxidation of benzyl alcohol can be calculated.

Effects of the ratio of the catalyst to benzyl alcohol: Catalytic activity of the Cu-based metal-organic framework toward the oxidation of benzyl alcohol to benzaldehyde by choosing different molar ratio [catalyst]/[substrate] was first investigated. As showing in Fig. 2, the reaction rate of oxidation of benzyl alcohol increased dramatically with increasing the molar ratio of metal-organic framework to the benzyl alcohol. This is because the catalytic sites increase accordingly with increasing molar ratio of catalyst to the substrate.

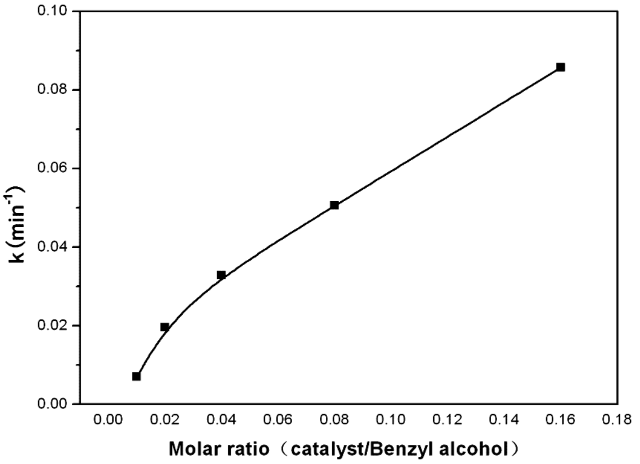

Fig. 2. Apparent first-order rate constants k (min^{-1}) for the oxidation of benzyl alcohol in different ratio of the catalyst to benzyl alcohol

Effects of temperature: In order to have a better understanding on the oxidation of benzyl alcohol catalyzed by $[Cu_3(BTC)_2(H_2O)_3]_n$, additional kinetic experiments were also carried out at different reaction temperature and the results were listed in Table-1. The oxidation reaction of benzyl alcohol in the presence of *Tris*-HCl buffer catalyzed by metal-organic framework with molar ratio of 0.04 was carried out. It can be found that the rate constant increased remarkably with an increase in the reaction temperature in all cases. This can be easily explained to the fact that it is helpful for molecular movement, the rate of adsorption and desorption of the reactant and product with the increasing of temperature.

TABLE-1
APPARENT FIRST-ORDER RATE CONSTANTS k (min^{-1}) FOR THE OXIDATION OF BENZYL ALCOHOL CATALYZED WITH IN DIFFERENT TEMPERATURE BY $[Cu_3(BTC)_2(H_2O)_3]_n^a$

Catalyst	k_{70}	k_{75}	k_{80}	k_{85}	k_{90}
$[Cu_3(BTC)_2(H_2O)_3]_n$	0.007	0.016	0.033	0.052	0.071

[a] pH = 7.8 Tris-HCl buffer, $C_{benzyl\ alcohol} = 1 \times 10^{-4}$ mol L^{-1}.

The oxidation of benzyl alcohol using hydrogen peroxide in the absence of the catalyst can be regarded as an Arrhenius-type process. The rate constant k could be expressed as $k = A \exp(-E_a/RT)$, where A is the Arrhenius pre-exponential constant and T the reaction temperature. Consequently, the nature logarithm of the rate constant can be presented as a linear function of 1/T. According to the linear regression, the slope of each straight line gives its E_a and the intercept gives A. Plots of ln k *versus* 1/T were obtained using the experimental data obtained at different temperatures and the plots obtained in measurements were straight line and regression coefficient was close to 1. This result indicates that the linear relationship between ln k and 1/T is good. Values of E_a were summarized in Table-2 and a representative Arrhenius plot of ln k *versus* 1/T for the oxidation reaction catalyzed by $[Cu_3(BTC)_2(H_2O)_3]_n$ was also shown in Fig. 3. As can be seen from Table-2, the calculated E_a for oxidation of benzyl alcohol in the absence of catalyst is *ca.* 120.69 kJ mol^{-1}.

TABLE-2
KINETIC PARAMETERS FOR REACTIONS OF BENZYL ALCOHOL CATALYZED BY $[Cu_3(BTC)_2(H_2O)_3]_n$, pH = 7.8 Tris-HCl BUFFER, $C_{benzyl\ alcohol} = 1\times10^{-4}$ mol L^{-1}

Catalyst	E_a (kJ mol^{-1})	A (g m^{-2} h^{-1})	R
$[Cu_3(BTC)_2(H_2O)_3]_n$	120.69	1.97×10^{16}	0.985

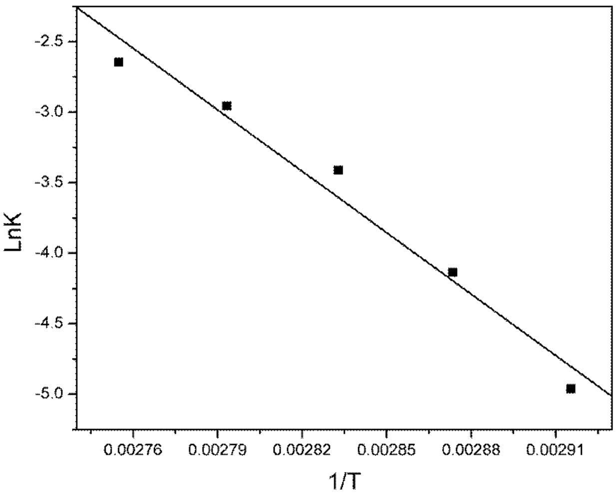

Fig. 3. Arrhenius plot of ln k *versus* 1/T for the oxidation reaction

Conclusion

Catalytic oxidation of benzyl alcohol catalyzed by $[Cu_3(BTC)_2(H_2O)_3]_n$ metal-organic framework was investigated kinetically in the presence of hydrogen peroxide. $[Cu_3(BTC)_2(H_2O)_3]_n$ showed higher catalytic activity, which is due to the fact that channel with larger diameter is advantageous for the catalytic reaction. Values of k_{obs} were found to increase with increasing the reaction temperature, molar ratio of catalyst/benzyl alcohol. Some of the parameters such as E_a and A were also estimated on the basis of the experimental data.

ACKNOWLEDGEMENTS

This work was supported by the Scientific Research & Development Foundation of Hefei University (No. 10KY14ZR), the NSFC (Nos. 20971001, 10979014, 51102073) and the Natural Science Foundation of Anhui Province (No. 10040606Q53) and the Natural Science Foundation of Educational Committee of Anhui Province (No. KJ2011A247).

REFERENCES

1. J.Z. Gu, W.G. Lu, L. Jiang, H.C. Zhou and T.B. Lu, *Inorg. Chem.*, **46**, 5835 (2007).
2. F.X.L. Xamena, A. Corma and H. Garcia, *J. Phys. Chem. C*, **111**, 80 (2007).
3. B.E. Logan, S.E. Oh, I.S. Kim and S. van Ginkel, *Environ. Sci. Technol.*, **36**, 2530 (2002).
4. K.C. Szeto, C. Prestipino, C. Lamberti, A. Zecchina, S. Bordiga, M. Bjørgen, M. Tilset and K.P. Lillerud, *Chem. Mater.*, **19**, 211 (2007).
5. J.T. Jankowiak and M.A. Barteau, *J. Catal.*, **236**, 366 (2005).
6. Z.X. Yang, Y.D. Xia and R. Mokaya, *Adv. Mater.*, **16**, 727 (2004).
7. L.G. Qiu, T. Xu, Z.Q. Li, W. Wang, Y. Wu, X. Jiang, X.Y. Tian and L.D. Zhang, *Angew. Chem. Int. Ed.*, **47**, 9487 (2008).