Available online at www.sciencedirect.com

SciVerse ScienceDirect

Chinese Chemical Letters 23 (2012) 53–56

CHINESE CHEMICAL LETTERS

www.elsevier.com/locate/cclet

# Liquid-phase epoxidation of styrene with $O_2$ over alkali metal salt impregnated CoAPO-5

Xiu Feng Shi [a], Bao Ping Shi [b], Bin Bin Fan [a,*], Rui Feng Li [a,*]

[a] Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, China
[b] College of Chemical and Biological Engineering, Taiyuan University of Science and Technology, Taiyuan 030021, China

Received 20 June 2011
Available online 8 November 2011

## Abstract

Liquid-phase epoxidation of styrene with atmospheric $O_2$ was conducted over CoAPO-5 molecular sieves. The catalytic performance of CoAPO-5 can be significantly improved by alkali metal salt impregnated on it, and styrene conversion and selectivity to styrene oxide reached 85% and 69% respectively when CsCl was impregnated on it. The catalyst was recyclable and exhibited similar catalytic activity and selectivity even after three catalytic reaction cycles.

*Keywords:* CoAPO-5; Styrene epoxidation; Oxygen; Alkali metal salt

Styrene oxide (SO) is an important commercial intermediate for the synthesis of fine chemicals and pharmaceuticals. Heterogeneous catalytic epoxidation of styrene with molecular oxygen as terminal oxidant in the absence of a sacrificial compound has attracted much interest [1–5]. In this aspect, cobalt-containing molecular sieves showed potential. It was reported that $Co^{2+}$-exchanged faujasite-type zeolites are active and selective for the epoxidation of styrene with $O_2$ in the absence of a co-reductant, and styrene conversion and SO selectivity reached 46% and 63% respectively [6]. Introduction of co-cations of $Ca^{2+}$, $Ba^{2+}$ and $Sr^{2+}$ to $Co^{2+}$-exchanged faujasite-type zeolites could further increase the styrene conversion and SO selectivity to 99% and 85% respectively [7].

Although CoAPO-n molecular sieves have been used to catalyze the oxidation of *p*-cresol [8], ethane [9] and cyclohexane [10,11] *etc.*, they are seldom applied in the epoxidation of alkenes with $O_2$. Only recently, R.V. Jasra *et al.* applied the Co-substituted SSZ-51 in the epoxidation of styrene with $O_2$. Co-SSZ-51 gave a styrene conversion and a SO selectivity of 50% and 70 – 80% respectively [12]. In order to explore the applied prospect of Co-substituted APO-n in the epoxidation of alkenes with $O_2$, in this communication, we report the epoxidation of styrene with $O_2$ over alkali metal salt impregnated CoAPO-5.

## 1. Experimental

CoAPO-5 molecular sieve was synthesized according to the method described in the reference [13]. The as-synthesized CoAPO-5 was calcined at 550 °C for 5 h to remove the organic template. The Co content in the calcined

---

* Corresponding authors.
*E-mail addresses:* fanbinbin@tyut.edu.cn (B.B. Fan), rfli@tyut.edu.cn (R.F. Li).

1001-8417/$ – see front matter
doi:10.1016/j.cclet.2011.09.027

CoAPO-5 was 2.7 wt.%. Alkali metal salt (LiCl, NaCl, KCl or CsCl) was impregnated on calcined CoAPO-5 by incipient wetness impregnation method. This was followed by drying at 100 °C for 12 h and calcining at different temperatures for 5 h. The obtained samples were denoted as M/CoAPO-5 (M = Li, Na, K or Cs).

The metal content was measured on an inductively coupled plasma-atomic emission spectrometer. X-ray diffraction (XRD) patterns were recorded on a Rigaku Dmax X-ray diffractometer with Ni-filtered CuKα radition. Diffuse reflectance UV–vis spectra in the range of 200–800 nm were measured against a halon white reference standard on a PE bio 40 UV-vis spectrophotometer equipped with an integration sphere.

The epoxidation of styrene with $O_2$ was carried out with a round-bottom glass flask. The liquid organic products were quantified with a gas chromatography equipped with a SE-30 capillary column and a FID detector using acetophenone as an internal standard.

## 2. Results and discussion

XRD measurements verified that all the M/CoAPO-5 samples are single phase with AFI structure because no obvious change in the position or the relative intensity of the diffraction lines for alkali metal salt impregnated CoAPO-5 was observed.

The diffuse reflectance (DR) UV–vis spectra of the as-synthesized, calcined and further alkali metal salt impregnated CoAPO-5 (calcined at 350 °C) are shown in Fig. 1. A very intense triplet band at 538, 583 and 630 nm with a shoulder band at 480 nm are observed in the spectrum of the as-synthesized sample, showing that most of the $Co^{2+}$ ions are tetrahedrally coordinated [14]. After calcination, two new absorption bands around 318 and 408 nm appeared at the expense of the triplet band. Different alternative interpretations have been proposed to explain the new bands. The new bands generally are attributed to a ligand-to-metal charge-transfer transition of $Co^{3+}$ ions formed upon oxidation of $Co^{2+}$ [15]. This is also proved by the result that these two bands completely disappeared, while the triplet band was recovered after reduction of the calcined CoAPO-5 with $H_2$ [16]. Furthermore, EXAFS studies indicate that about 20% of framework $Co^{2+}$ could be oxidized to $Co^{3+}$ during calcination process [17]. Unexpectedly, the intensity of the two bands also markedly decreased for the M/CoAPO-5. It was reported that part of tetrahedrally coordinated Co configurations possibly deformed during the calcination process, resulting in the color change from blue to yellow greenish and giving two bands around 320 and 410 nm [18]. This suggests that the deformation degree of tetrahedral Co site might be considerably decreased after impregnation of alkali metal salts, probably because of the existence of an interaction between alkali metal cations and tetrahedrally coordinated $Co^{2+}$ species since $Co^{3+}$ species cannot be reduced by alkali metal salts.

The catalytic results obtained in the epoxidation of styrene with $O_2$ over CoAPO-5 and M/CoAPO-5 were summarized in Table 1. In all cases, the mass balances for all the samples are above 95% with SO, phenylacetaldehyde (PA) and benzaldehyde (BA) as the major products. CoAPO-5 (entry 2) gave a styrene conversion and a selectivity to

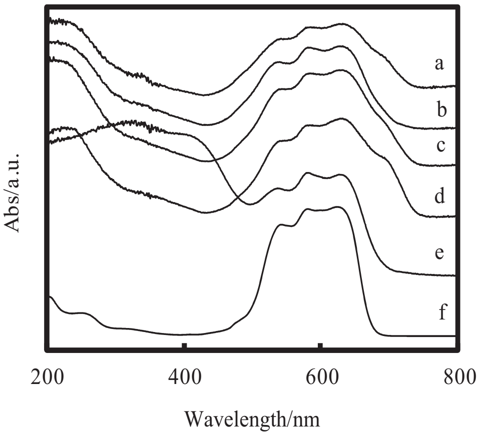

Fig. 1. UV–vis spectra of calcined Cs/CoAPO-5 (a), K/CoAPO-5 (b), Na/CoAPO-5 (c), Li/CoAPO-5 (d), CoAPO-5 (e) and as-synthesized CoAPO-5 (f).

Table 1
Catalytic results for the epoxidation of styrene with $O_2$ over CoAPO-5 and M/CoAPO-5.

| Entry | Catalyst | M/Co (mol/mol) | Calcined temperature (°C) | Solvent | Conversion (%) | Product selectivity (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | BA | PA | SO |
| 1 | Blank | – | – | Dioxane | 21 | 84 | 4.0 | 12 |
| 2 | CoAPO-5 | 0 | – | Dioxane | 38 | 53 | 10 | 37 |
| 3 | Li/CoAPO-5 | 1.0 | 350 | Dioxane | 74 | 27 | 18 | 55 |
| 4 | Na/CoAPO-5 | 1.0 | 350 | Dioxane | 81 | 23 | 21 | 56 |
| 5 | K/CoAPO-5 | 1.0 | 350 | Dioxane | 82 | 12 | 22 | 66 |
| 6 | Cs/CoAPO-5 | 1.0 | 350 | Dioxane | 85 | 12 | 19 | 69 |
| 7 | Cs/CoAPO-5 | 0.5 | 350 | Dioxane | 69 | 17 | 23 | 60 |
| 8 | Cs/CoAPO-5 | 0.8 | 350 | Dioxane | 77 | 12 | 21 | 67 |
| 9 | Cs/CoAPO-5 | 1.5 | 350 | Dioxane | 80 | 14 | 21 | 65 |
| 10 | Cs/CoAPO-5 | 1.0 | 350 | DMF | 50 | 26 | 8 | 66 |
| 11 | Cs/CoAPO-5 | 1.0 | 350 | Cyclohexanone | 70 | 34 | 17 | 49 |
| 12 | Cs/CoAPO-5 | 1.0 | 350 | Trioxane | 72 | 24 | 18 | 58 |
| 13 | Cs/CoAPO-5 | 1.0 | 100 | Dioxane | 75 | 9 | 32 | 59 |
| 14 | Cs/CoAPO-5 | 1.0 | 550 | Dioxane | 80 | 23 | 25 | 52 |
| 15 | Cs/CoAPO-5$^{\text{2nd}}$ | 1.0 | 350 | Dioxane | 82 | 12 | 17 | 71 |
| 16 | Cs/CoAPO-5$^{\text{3rd}}$ | 1.0 | 350 | Dioxane | 84 | 12 | 17 | 71 |
| 17 | Co/APO-5[a] | – | – | Dioxane | 68 | 24 | 25 | 51 |
| 18 | Cs/Co/APO-5 | 1.0 | 350 | Dioxane | 88 | 19 | 55 | 26 |

Reaction conditions: 0.1 g catalyst, 10 mL solvent, 5 mmol styrene, 10 mL/min $O_2$, 100 °C, 4 h.

[a] Prepared by impregnation of Co salt on AlPO-5 and calcining at 550 °C for 5 h. Co content: 2.7 wt.%.

SO of 38% and 37% respectively, which are much higher than those of blank experiment (entry 1). Impregnation of alkali metal salts on the CoAPO-5 led to a significant increase in both the catalytic activity and the selectivity, which, moreover, increased with increasing alkalinity of alkali metal salts (entries 3–6). Cs/CoAPO-5 showed a styrene conversion and a selectivity to SO of 85% and 69% respectively, which are comparable to those of the alkali metal or alkali earth metal ion-exchanged Co–NaX [7]. Although the promotional effect of alkali metal salts on the catalytic performance of CoAPO-5 is not very clear, we speculate that it might result from the interaction between alkali metal cations and Co species, which weaken the distortion extent of tetrahedral $Co^{2+}$ caused by removal of template during calcination. In addition, the promotion effect is closely related to the methods of introduction of Co species into APO-5. For Co-impregnated APO-5 (Co/APO-5), the impregnated CsCl could also increase styrene conversion and decrease BA selectivity as it did for CoAPO-5, but it greatly promoted PA formation at the expense of SO (entries 17, 18).

The catalytic performance of Cs/CoAPO-5 was highly dependent on the solvent and the calcination temperature employed after impregnation of alkali metal salts. 1,4-Dioxane as solvent was much more active and selective than DMF, trioxane and cyclohexanone (entries 3, 10–12). This is different from that observed over Co–NaX and its alkali metal or alkaline earth metal ion-exchanged analogues, which showed high activity and SO selectivity in DMF solvent. The difference may be related to their different Co environment. $Co^{2+}$ is located in the ion-exchange position for the Co–NaX, while it is sited in the framework for the CoAPO-5. Despite that the selectivity to SO and PA of Cs/CoAPO-5 decreased with increasing calcination temperature, its activity exhibited a volcanic trend (entries 3, 13, 14). Considering the activity and selectivity, the sample should be calcined at 350 °C.

The Cs/Co molar ratio (entries 3, 7–9) also strongly influenced the catalytic performance of Cs/CoAPO-5. The activity and selectivity both increased with increasing Cs/Co molar ratio up to 1.0. A further increase in the Cs/Co molar ratio had no positive effect.

Table 1 also shows that Cs/CoAPO-5 (Cs/Co = 1.0, calcined at 350 °C) had high stability (entries 15, 16). Its catalytic activity was kept at least within three repeated runs with regeneration (the catalyst was recovered from the reaction mixture by centrifuging and washing with acetone). Neither Co nor Cs was detected in the reaction liquid. This shows that Cs/CoAPO-5 is recyclable. This could be attributed to the incorporation of $Co^{2+}$ in the framework of CoAPO-5.

In conclusion, alkali metal salt impregnated CoAPO-5 is a highly active, selective and stable heterogeneous catalyst for the liquid phase epoxidation of styrene with $O_2$. The activity and selectivity to SO and PA increased with increasing alkalinity of alkali metal salts. The catalytic performance of Cs/CoAPO-5 is also highly dependent on the Cs/Co molar ratio, the employed solvent and the calcination temperature after impregnation of alkali metal salts.

## Acknowledgments

This work is supported by the National Natural Science Foundation of China (No. 20971095), the Science Foundation of Shanxi Province (No. 2010011014-4) and the Foundation for Returned Overseas Scholars of Shanxi Province (No. 2008-10).

## References

[1] Z. Opre, T. Mallat, A. Baiker, J. Catal. 245 (2007) 482.
[2] S. Bhattacharjee, J.A. Anderson, J. Mol. Catal. A: Chem. 249 (2006) 103.
[3] H.J. Zhan, Q.H. Xia, X.H. Lu, et al. Catal. Commum. 8 (2007) 1472.
[4] B. Tyagi, B. Shaik, H.C. Bajaj, Appl. Catal. A: Gen. 383 (2010) 161.
[5] A. Corma, I. Domínguez, A. Doménech, et al. J. Catal. 265 (2009) 238.
[6] Q.H. Tang, Q.H. Zhang, H.L. Wu, et al. J. Catal. 230 (2005) 384.
[7] J. Sebastian, K.M. Jinka, R.V. Jasra, J. Catal. 244 (2006) 208.
[8] D.S. Kim, S.H. Chang, W.S. Ahn, J. Mol. Catal. A: Chem. 179 (2002) 175.
[9] P. Concepción, J.M. López Nieto, Catal. Commun. 2 (2001) 363.
[10] R. Raja, G. Sankar, J.M. Thomas, J. Am. Soc. Chem. 121 (1999) 11926.
[11] P. Selvam, S.K. Mohapatra, J. Catal. 233 (2005) 276.
[12] K.M. Jinka, S.M. Pai, B.L. Newalkar, et al. Catal. Commun. 11 (2010) 638.
[13] W.B. Fan, B.B. Fan, M.G. Song, et al. Micropor. Mesopor. Mater. 94 (2006) 348.
[14] C. Montes, M.E. Davis, B. Murray, et al. J. Phys. Chem. 94 (1990) 6425.
[15] Q. Gao, B.M. Weckhuysen, R.A. Schoonheydt, Micropor. Mesopor. Mater. 27 (1999) 75.
[16] M.S. Jeong, H. Frei, J. Mol, J. Catal. A: Chem. 156 (2000) 245.
[17] P.A. Barrett, G. Sankar, C.R.A. Catlow, et al. J. Phys. Chem. 100 (1996) 8977.
[18] J. Šponer, J. Čejka, J. Dědeček, et al. Micropor. Mesopor. Mater. 37 (2000) 117.