Boron-modified Chlorine-free K^+–FeO_x/SBA-15 as Highly Effective Catalyst for Propylene Epoxidation by Nitrous Oxide

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Modification of chlorine-free alkali metal ion (K^+, Rb^+, or Cs^+)-containing FeO_x/SBA-15 catalysts with boron enhanced their catalytic performances in propylene epoxidation by nitrous oxide. A B–K^+–FeO_x/SBA-15 catalyst (K/Fe = 2.5, B/Fe = 0.5) showed the best propylene oxide (PO) formation activity, providing PO selectivities of 79 and 55% at propylene conversions of 4.8 and 13% at 350 and 400 °C, respectively.

The epoxidation of propylene using a "green" oxidant has attracted much attention in recent years.[1] Although oxygen or air is the most ideal oxidant, the epoxidation of C_3H_6 by O_2 is still not successful, and PO selectivity can hardly exceed 60% even at a low C_3H_6 conversion.[2] A few efficient catalysts have been reported for the epoxidation of C_3H_6 by H_2O_2 in liquid phase,[3] but the high cost of H_2O_2 and the difficulty in its handling are problems. Many studies have contributed to the in situ production of H_2O_2 from O_2–H_2 gas mixture for C_3H_6 epoxidation.[4] Among the catalysts reported, the Au–Ti-based vapor-phase catalysts developed by Haruta and co-workers have attracted much attention.[4b–4d]

Recently, we studied an iron-based C_3H_6 epoxidation catalytic system with N_2O as the oxidant.[5] We reported that a KCl-modified 1 wt % FeO_x/SBA-15 (K/Fe = 5) catalyst could provide PO selectivities of 72 and 50% at C_3H_6 conversions of 4.5 and 10%, respectively.[5a,5b] However, the use of other potassium salt such as KAc as the modifier led to remarkably lower PO formation activities.[5b] Because chlorine may go to the gas phase to act as a radical promoter and may be lost during the reaction, it is useful to develop a highly efficient chlorine-free catalyst. Herein, we report our recent finding that the presence of boron can significantly enhance the catalytic properties of the no-chlorine K^+ (Rb^+ or Cs^+)–FeO_x/SBA-15 catalysts.

SBA-15 and FeO_x/SBA-15 were prepared using the procedure reported previously.[5b] The modified FeO_x/SBA-15 catalysts were prepared by impregnation of the FeO_x/SBA-15 powder with an aqueous solution of alkali metal acetate or a mixed aqueous solution containing alkali metal acetate and H_3BO_3 in a fixed ratio, followed by drying and calcination at 823 K for 6 h. The contents of iron and potassium in the catalysts were determined by ICP. The catalysts were characterized by XRD and N_2 sorption. Catalytic reactions were carried out using a fixed-bed flow reactor (quartz tube) operated at atmospheric pressure. The products were analyzed by two on-line gas chromatographs.

Table 1 shows the catalytic performances of the 1 wt % FeO_x/SBA-15 catalysts modified by various alkali metal ions with and without boron for the epoxidation of C_3H_6 by N_2O. It should be noted that no reaction occurred without iron irrespective of the presence or absence of boron or alkali metal ions on SBA-15. In the absence of an alkali metal ion, no formation of PO was observed over the FeO_x/SBA-15 or the B–FeO_x/SBA-15. The modification with a no-halogen alkali metal ion could also induce the PO formation and enhance C_3H_6 conversion. Among the alkali metal ions, Na^+ and K^+ showed similar enhancing effects and were better than Li^+, Rb^+, and Cs^+ as modifiers. As compared with the KCl–FeO_x/SBA-15 catalyst reported previously,[5a] the present chlorine-free K^+–FeO_x/SBA-15 catalyst exhibited a lower C_3H_6 conversion and a lower PO selectivity. However, the presence of boron remarkably increased the PO selectivities as well as C_3H_6 conversions for the K^+-, Rb^+-, and Cs^+-modified FeO_x/SBA-15 catalysts although the catalytic performances of the Li^+– and Na^+–FeO_x/SBA-15 catalysts were not obviously altered by boron. PO selectivities over the B- and K^+ (Rb^+ or Cs^+)-doubly modified catalysts were higher than 70%. Similar to other catalysts,[5,6] the activity of the present catalyst also decreased with time on stream (TOS), but the activity can be recovered by regenerating the catalyst with a gas flow containing O_2 at 823 K (Table 1).

Table 1. Effect of boron on catalytic results of alkali metal ion-modified FeO_x/SBA-15 for C_3H_6 epoxidation by N_2O[a]

Catalyst[b]	C_3H_6 conv. /%	Selectivity/%		
		PO	Others[c]	CO_x
FeO_x/SBA-15	1.3	0	50	50
B–FeO_x/SBA-15	2.3	0	59	41
Li^+–FeO_x/SBA-15	4.1	16	62	22
B–Li^+–FeO_x/SBA-15	3.5	16	60	24
Na^+–FeO_x/SBA-15	4.2	69	18	13
B–Na^+–FeO_x/SBA-15	4.4	66	21	13
K^+–FeO_x/SBA-15	3.8	64	14	22
B–K^+–FeO_x/SBA-15	4.8	79	12	9.4
B–K^+–FeO_x/SBA-15[d]	1.6	80	11	8.9
B–K^+–FeO_x/SBA-15[e]	4.9	77	12	11
B–K^+–FeO_x/SBA-15[f]	8.9	68	14	18
B–K^+–FeO_x/SBA-15[g]	13	55	15	30
Rb^+–FeO_x/SBA-15	2.9	54	13	33
B–Rb^+–FeO_x/SBA-15	4.2	74	13	13
Cs^+–FeO_x/SBA-15	2.8	45	18	37
B–Cs^+–FeO_x/SBA-15	4.4	76	14	10

[a]Reaction conditions: W(catalyst) = 0.2 g, T = 350 °C, $P(C_3H_6)$ = 2.5 kPa, $P(N_2O)$ = 25.3 kPa, F(total) = 60 mL min^{-1}, TOS = 30 min. [b]Fe content = 1 wt %; alkali metal ion/Fe (molar ratio) = 2.5, B/alkali metal ion (molar ratio) = 0.5. [c]Others include acrolein, allyl alcohol, acetone, and acetaldehyde. [d]TOS = 230 min. [e]Regenerating the catalyst after 230 min of reaction, followed by reaction for 30 min. [f]T = 375 °C. [g]T = 400 °C.

We have carried out further studies on the effect of boron on catalytic performances of the K^+–FeO_x/SBA-15 catalysts with

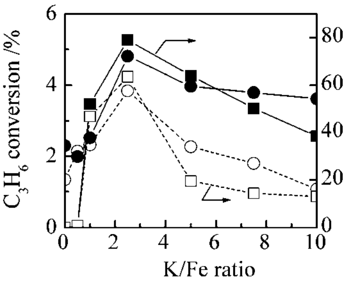

Figure 1. Effect of boron on catalytic behavior of K^+–1 wt % FeO_x/SBA-15 catalysts with different K/Fe ratio (B/K = 0.5). (○) and (●), C_3H_6 conversion; (□) and (■), PO selectivity. Solid and dashed lines are for the catalysts with and without boron modification, respectively. Reaction conditions are the same as those in Table 1.

different K/Fe ratio. Figure 1 shows that, in the absence of boron modification, both C_3H_6 conversion and PO selectivity reach maximum values at a K/Fe ratio of 2.5, and further increases in the K/Fe ratio decrease the PO selectivity steeply. The conversion of C_3H_6 also dropped at the same time. The addition of boron into the K^+–FeO_x/SBA-15 catalysts with K/Fe ratios of 0.5 and 1.0 did not obviously change the catalytic performances. However, for the K^+–FeO_x/SBA-15 catalysts with K/Fe ratios of $\geq$2.5, the presence of boron increased the catalytic performances significantly. Further studies with the B–K^+–1 wt % FeO_x/SBA-15 (K/Fe = 2.5) by varying boron content confirmed that the catalyst with a B/K ratio of 0.5 exhibited the best performance for PO formation. PO selectivity was 79% at a C_3H_6 conversion of 4.8% over this catalyst at 350 °C. By increasing the temperature to 375 and 400 °C, C_3H_6 conversions rose to 8.9 and 13%, and PO selectivities could be maintained at 68 and 55%, respectively. These values are even better than those reported for the KCl–FeO_x/SBA-15 catalyst and other iron-based catalysts.[5a,6]

To clarify why the presence of boron can exert such a positive role in raising the catalytic performances of the K^+ (Rb^+ or Cs^+)–FeO_x/SBA-15 catalyst, we have investigated the influence of boron on catalyst structures. N_2-sorption measurements showed that the addition of Li^+, Na^+, K^+, Rb^+, and Cs^+ to the 1 wt % FeO_x/SBA-15 sample decreased BET surface areas from 684 to 444, 403, 269, 290, and 279 $m^2\,g^{-1}$, respectively. This change indicates that the alkali metal ions, especially those with strong basicity such as K^+, Rb^+, and Cs^+, may partially destroy the mesoporous structure of SBA-15 via the reaction with the silica wall. The modification of boron raised the BET surface areas of the K^+-, Rb^+-, and Cs^+-modified samples to 332, 372, and 363 $m^2\,g^{-1}$, respectively, but did not increase those of the Li^+- and Na^+-modified samples. Thus, boron may restore the ordered mesoporous structure to some extent through the interaction with K^+, Rb^+, or Cs^+. Such effect of boron was also observed for the K^+–FeO_x/SBA-15 catalysts with different K/Fe ratios. As shown in Figure 2, the change in XRD patterns after the addition of boron to the sample with a K/Fe ratio of 5 clearly suggests that the partially destroyed ordered mesoporous structure is restored by boron modification.

However, the modification with other acidic groups such as phosphate and sulfate did not increase the catalytic performances of the K^+–FeO_x/SBA-15 catalyst significantly although they could also restore the ordered mesoporous structure. We speculate that boron may have other functions such as improving the electrophilicity of the oxygen species derived from N_2O because of the electron-deficient nature of boron. Boron may also regulate the acid–base property of the catalyst, which may affect the consecutive conversion of PO. Our XPS studies suggest that boron is in +III state. As for the location of boron, we speculate that boron may be located inside the mesoporous channels and has strong interactions with both alkali metal ions and iron species.

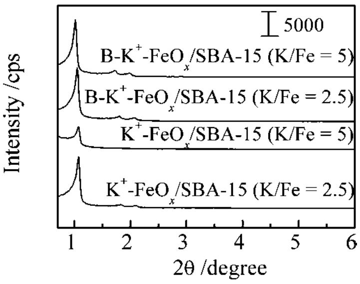

Figure 2. XRD patterns of the K^+–1 wt % FeO_x/SBA-15 samples with (B/K = 0.5) and without boron.

In conclusion, we have found an interesting enhancing effect of boron on the catalytic performance of the FeO_x/SBA-15 catalysts modified by K^+, Rb^+, or Cs^+ for PO formation. The chlorine-free B–K^+–FeO_x/SBA-15 catalyst can provide better PO formation activity than the KCl–FeO_x/SBA-15 catalyst.

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References

1 T. A. Nijhuis, M. Makkee, J. A. Moulijn, B. M. Weckhuysen, *Ind. Eng. Chem. Res.* **2006**, *45*, 3447.
2 For recent references on C_3H_6 epoxidation by O_2, see for examples: a) J. Lu, J. J. Bravo-Suárez, A. Takahashi, M. Haruta, S. T. Oyama, *J. Catal.* **2005**, *232*, 85. b) J. Lu, J. J. Bravo-Suárez, M. Haruta, S. T. Oyama, *Appl. Catal. A* **2006**, *302*, 283. c) N. Mimura, S. Tsubota, K. Murata, K. K. Bando, J. J. Bravo-Suarez, M. Haruta, S. T. Oyama, *Catal. Lett.* **2006**, *110*, 47. d) H. Chu, L. Yang, Q. Zhang, Y. Wang, *J. Catal.* **2006**, *241*, 225.
3 a) M. G. Clerici, G. Bellussi, U. Romano, *J. Catal.* **1991**, *129*, 159. b) X. Zuwei, Z. Ning, S. Yu, L. Kunlan, *Science* **2001**, *292*, 1139. c) K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964.
4 a) R. Meiers, U. Dingerdissen, W. F. Hölderich, *J. Catal.* **1998**, *176*, 376. b) T. Hayashi, K. Tanaka, M. Haruta, *J. Catal.* **1998**, *178*, 566. c) A. K. Sinha, S. Seelan, S. Tsubota, M. Haruta, *Top. Catal.* **2004**, *29*, 95. d) A. K. Sinha, S. Seelan, M. Okumura, T. Akita, S. Tsubota, M. Haruta, *J. Phys. Chem. B* **2005**, *109*, 3956.
5 a) X. Wang, Q. Zhang, Q. Guo, Y. Lou, L. Yang, Y. Wang, *Chem. Commun.* **2004**, 1396. b) X. Wang, Q. Zhang, S. Yang, Y. Wang, *J. Phys. Chem. B* **2005**, *109*, 23500. c) Q. Zhang, Q. Guo, X. Wang, T. Shishido, Y. Wang, *J. Catal.* **2006**, *239*, 105. d) Y. Wang, W. Yang, L. Yang, X. Wang, Q. Zhang, *Catal. Today* **2006**, *117*, 156.
6 a) V. Duma, D. Hönicke, *J. Catal.* **2000**, *191*, 93. b) E. Ananieva, A. Reitzmann, *Chem. Eng. Sci.* **2004**, *59*, 5509.