

Iron-catalysed propylene epoxidation by nitrous oxide: dramatic shift of allylic oxidation to epoxidation by the modification with alkali metal salts

Xiaoxing Wang, Qinghong Zhang, Qian Guo, Yinchuan Lou, Lüjuan Yang and Ye Wang*

State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, P. R. China. E-mail: yewang@jingxian.xmu.edu.cn; Fax: (+86)-592-2183047; Tel: (+86)-592-2187470

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A dramatic shift of allylic oxidation to epoxidation has been observed during the oxidation of propylene by N_2O when the $FeO_x/SBA-15$ catalyst is modified with alkali metal salts, and the roles of alkali metal salts are to suppress the reactivity of lattice oxygen and to induce an iron coordination structure effective for epoxidation with N_2O .

The epoxidation of propylene to propylene oxide (PO) is one of the most challenging chemical reactions. Although TS-1 and Pd/TS-1 can catalyze this reaction efficiently in liquid phase with H_2O_2 and O_2-H_2 gas mixture, respectively,^{1,2} only a few studies have succeeded in achieving high efficiency for the gas phase epoxidation of C_3H_6 .³ Unlike C_2H_4 , because C_3H_6 possesses allylic hydrogen, the easy abstraction of this hydrogen in the gas phase reaction usually results in allylic intermediates leading to allylic oxidation and further deep oxidation. There have been many attempts to use O_2 as an oxidant for the epoxidation of C_3H_6 , but high PO selectivity can only be obtained over a few catalysts.³ PO selectivity of ca. 90% has been reported when H_2 is co-fed with O_2 over Au-Ti-based catalysts, but the conversion of C_3H_6 and the efficiency of H_2 are still not satisfactory.⁴

On the other hand, there are incentives to exploit N_2O as an oxidant for selective oxidation reactions since the by-product of an oxidation reaction would be N_2 and the process would be environmentally benign. The selective oxidation of benzene to phenol with N_2O has been intensively studied over iron-containing ZSM-5.⁵ One of the present authors has found that CH_4 and C_2H_6 can be oxidized to the corresponding alcohols with N_2O over an iron phosphate catalyst.⁶ Reports on the use of N_2O for epoxidation of alkenes are, however, scarce.⁷

Recently, we investigated the catalytic property of an iron-containing SBA-15 catalyst for the gas phase oxidation of C_3H_6 with N_2O , and found an interesting shift of reaction pathway from allylic oxidation to epoxidation by the modification of the catalyst with an alkali metal salt such as KCl. Although a $Na^+-Fe_2O_3/SiO_2$ has been reported for the epoxidation of C_3H_6 , the role of the alkali metal ion is not clear.^{7c} Through our work, we have gained significant information about the factors controlling the reaction route to allylic oxidation or to epoxidation. In this communication, we report the dramatic shift of reaction route by the modification of the catalyst and the elucidation of the roles of the modifier.

SBA-15, a typical mesoporous silica, was synthesized with the procedures reported previously.⁸ The $FeO_x/SBA-15$ sample was prepared by an impregnation method using an ethanolic solution of $[Fe^{III}(acac)_3]$ (acac = acetylacetonate). After calcination at 823 K, the sample was further modified with alkali salt by the impregnation followed by drying and calcination at 823 K for 6 h. XPS measurements showed that the oxidation state of iron was III in the calcined $FeO_x/SBA-15$ and did not change after the modification with KCl. XRD and TEM studies confirmed that the ordered mesoporous structure of SBA-15 was sustained after the introduction of FeO_x (0–5 wt%) and KCl (K/Si = 0–0.12), but the surface area and pore volume determined by N_2 -sorption decreased gradually with an increase in the content of either iron or KCl, suggesting the filling of the mesoporous channels with FeO_x and KCl. That any crystalline phases of iron oxide and KCl were not observed for the KCl- $FeO_x/SBA-15$ (Fe, 0–5 wt%; K/Si, 0–0.12) indicated the high dispersions of both FeO_x and KCl. Catalytic

reactions were carried out using a fixed-bed flow reactor. The products were analyzed by two on-line gas chromatographs equipped with FID and TCD detectors, respectively. A Porapak T column connected to an FID detector was used for the analysis of C_3H_6 , PO and other oxygenated products.

Table 1 shows the results for the oxidation of C_3H_6 with N_2O over the $FeO_x/SBA-15$ with and without modification by KCl. SBA-15 with or without modification was always inactive in the absence of iron, suggesting that iron was the active site. Over the $FeO_x/SBA-15$ without KCl, acrolein was mainly formed in addition to CO_x (CO and CO_2), indicating the occurrence of the allylic oxidation of C_3H_6 . After the modification by KCl, PO became the main product over the samples with iron content lower than 3 wt%. PO selectivity decreased remarkably with an increase in iron content up to 5 wt% and only CO_x was observed over the KCl- Fe_2O_3 , strongly suggesting that highly dispersed iron sites are responsible for the epoxidation of C_3H_6 with N_2O . The sample with iron content of 1 wt% exhibited the highest performance for PO formation. This iron content is much higher than that in the $Na^+-Fe_2O_3/SiO_2$ catalyst (100–1000 ppm).^{7c} We have obtained better catalytic performances with such a relatively higher iron content probably because iron can be dispersed in a better way in the mesopores of SBA-15.

Fig. 1 shows the effect of KCl content in the 1 wt% $FeO_x/SBA-15$ on catalytic performances. The increase in the content of the modifier dramatically increased the selectivity to PO and decreased those to allylic oxidation and deep oxidation products. In other words, a dramatic shift from allylic oxidation to epoxidation took place by the modification of $FeO_x/SBA-15$ with KCl. Moreover, it is interesting that, with increasing K/Fe ratio, C_3H_6 conversion first decreased slightly but then underwent a remarkable rise and increased for more than four times as compared with the sample without modification.

Table 1 Selective oxidation of propylene with N_2O over $FeO_x/SBA-15$ and KCl-modified $FeO_x/SBA-15$

Catalyst	Conversion (%)	Selectivity (%)				
		PO	AL ^a	AA ^b	Others	CO _x
0.5 wt% $FeO_x/SBA-15$	0.65	0	57	3.7	7.3	32
1 wt% $FeO_x/SBA-15$	1.17	0	42	4.5	7.5	46
5 wt% $FeO_x/SBA-15$	1.32	0	36	2.6	7.4	54
Fe_2O_3	0.52	0	10	0	5.0	85
$K^+-0.5$ wt% FeO_x/SBA^c	2.59	76	1.8	1.1	6.1	15
K^+-1 wt% FeO_x/SBA^c	4.51	72	1.6	1.1	7.3	18
K^+-1 wt% FeO_x/SBA^d	1.87	81	1.8	0.5	4.7	12
K^+-1 wt% FeO_x/SBA^e	1.21	80	2.1	0.6	5.3	12
K^+-1 wt% FeO_x/SBA^f	3.77	77	1.7	0.5	6.8	14
K^+-3 wt% FeO_x/SBA^c	4.09	68	2.6	1.4	12	16
K^+-5 wt% FeO_x/SBA^c	5.80	14	7.8	1.2	37	40
$K^+-Fe_2O_3^g$	trace					100

Reaction conditions: $P(C_3H_6) = 2.5$ kPa, $P(N_2O) = 25.3$ kPa; $T = 598$ K; catalyst, 0.20 g; total flow rate, 60 ml min⁻¹; TOS, 30 min. ^a AL = acrolein. ^b AA = allyl alcohol. ^c K/Si = 0.04. ^d TOS, 110 min. ^e TOS, 190 min. ^f Regenerating the catalyst after 240 min of reaction, followed by reaction for 30 min. ^g K/Fe = 1.

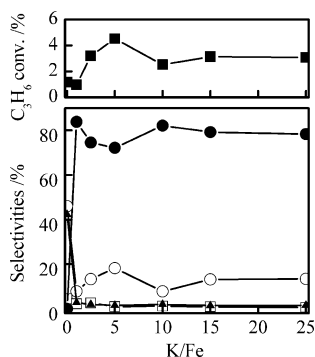


Fig. 1 Changes of catalytic performances with a change in K/Fe atomic ratio in the modified 1 wt% FeO_x/SBA-15. Symbols of selectivity: (●) propylene oxide, (□) allyl alcohol, (▲) acrolein, (○) CO_x.

Further investigations revealed that, similar shift of allylic oxidation to epoxidation likewise occurred when other potassium salts such as KNO₃, KAc or KBr were used as the modifier instead of KCl. Thus, it was K⁺ but not Cl⁻ played an important role. Other alkali metal salt such as LiCl, NaCl, RbCl or CsCl also worked as useful modifiers for PO formation. PO selectivity and yield decreased with the following sequence, KCl > NaCl > RbCl > CsCl > LiCl. By changing reaction conditions, PO selectivity of 80% can be obtained at 4% C₃H₆ conversion over a K⁺-FeO_x/SBA-15 catalyst, higher than that reported over the Na⁺-Fe₂O₃/SiO₂ catalyst (70% PO selectivity at 2.5% C₃H₆ conversion).^{7c} The turnover frequency for PO formation over our catalyst was 5.2 mol (mol-Fe)⁻¹ h⁻¹. Similar to many catalysts reported so far,^{3,4,7c} the activity of our catalyst also decreased with time on stream (TOS) as shown in Table 1. It has been clarified that the decrease in C₃H₆ conversion with TOS is caused by the carbon deposition, and the activity can almost be recovered by regenerating the catalyst with a gas flow containing He and O₂ at 823 K.

We have clarified that the redox property is an important factor in determining the reaction route. The H₂-TPR studies indicated that the reactivity of the lattice oxygen of FeO_x in the FeO_x/SBA-15 was remarkably inhibited by the modification with K⁺ (Fig. 2A). A reduction peak corresponding to the reduction of Fe³⁺ to Fe²⁺ was observed at 682 K for the sample without modification. The main reduction peak was shifted to 888–918 K after the modification

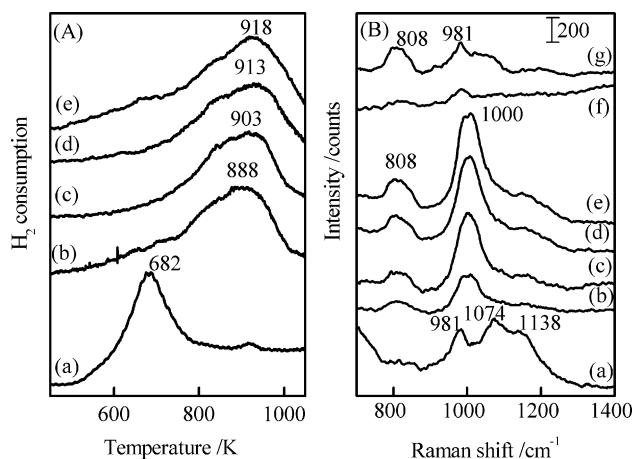


Fig. 2 TPR profiles (A) and UV-Raman spectra (B). (a) 1 wt% FeO_x/SBA-15, (b) K⁺-1 wt% FeO_x/SBA-15 (K/Fe = 2.5), (c) K⁺-1 wt% FeO_x/SBA-15 (K/Fe = 5), (d) K⁺-1 wt% FeO_x/SBA-15 (K/Fe = 10), (e) K⁺-1 wt% FeO_x/SBA-15 (K/Fe = 15), (f) SBA-15, (g) K⁺/SBA-15 (K/Si = 0.04).

with K⁺. This corresponds to the inhibition of the allylic oxidation and is consistent with the consensus that the nucleophilic lattice oxygen species generally attack the allylic hydrogen and induce allylic oxidation. In other words, one role of K⁺ is to inhibit the reactivity of lattice oxygen and thus to suppress the allylic oxidation.

Because not only PO selectivity but C₃H₆ conversion also increased remarkably after the addition of K⁺, the presence of K⁺ must also accelerate the activation of N₂O for C₃H₆ epoxidation. Our investigations have suggested that the change in the coordination structure of iron brought by K⁺ may account for such an accelerating effect. A distinct Raman band at ca. 1000 cm⁻¹ was observed after the modification of the FeO_x/SBA-15 with an alkali metal salt in UV-Raman studies, which have been shown to be useful in determining the coordination structure of iron.⁹ In Fig. 2B, the FeO_x/SBA-15 showed Raman bands at 981, 1074 and 1138 cm⁻¹ in the region of 900–1200 cm⁻¹. The latter two bands probably arise from the tetrahedral iron site in the framework of SBA-15. A part of iron may be incorporated into the framework of SBA-15 in the FeO_x/SBA-15. After the modification with K⁺, these bands became unnoticeable, and a band at 1000 cm⁻¹ appeared distinctly. Another band at 808 cm⁻¹ also appeared after the modification with K⁺, but this band could also be observed for a K⁺/SBA-15 without iron (curve g of Fig. 2B). Thus, the band at 808 cm⁻¹ may not be related to iron sites. The intensity of the band at 1000 cm⁻¹ increased with an increase in K/Fe ratio from 0 to 5.0, and slightly decreased with a further increase in K/Fe ratio. Since this band shifts slightly to a lower wavenumber as compared with those assigned to the framework Fe–O–Si, we tentatively speculate that it arises from the tetrahedral FeO₄ on the surface, which is probably stabilized by alkali ions. Such an iron structure should be effective for the activation of N₂O for the epoxidation of C₃H₆.

In conclusion, we have found a dramatic shift of reaction route from allylic oxidation to epoxidation during the oxidation of propylene with N₂O by modifying the FeO_x/SBA-15 with K⁺. The roles of K⁺ are to suppress the allylic oxidation by decreasing the reactivity of lattice oxygen and to induce a coordination structure of iron effective for epoxidation.

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