

Co²⁺-Exchanged faujasite zeolites as efficient heterogeneous catalysts for epoxidation of styrene with molecular oxygen

Qinghu Tang, Ye Wang,* Jun Liang, Ping Wang, Qinghong Zhang and Huilin Wan

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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Co²⁺-Exchanged faujasite zeolites can efficiently catalyze the epoxidation of styrene with molecular oxygen, and the Co²⁺ ions located in supercages are suggested to account for the activation of O₂ for the epoxidation of styrene.

Molecular oxygen is the most desirable oxidant for the epoxidation of alkenes with respect to environmental and economic consideration. However, little success has been achieved for the selective epoxidation of alkenes with O₂ except for ethylene. Cobalt ions and complexes are well-known catalysts for the selective oxidation of alkanes and alkylbenzenes with O₂.¹ Cobalt complexes have also been used for the epoxidation of alkenes with *tert*-butyl hydroperoxide and iodossylbenzene,² but the studies on exploitation of cobalt catalysts for the epoxidation of alkenes with O₂ as oxidant are scarce. The autooxidation of alkenes in O₂ with the first-row transition metal compound typically resulted in a high degree of oxidized polymers as well as cleaved products.³ Drago and co-workers reported the catalytic oxidation of terminal olefins including styrene by O₂ to the corresponding 2-ketones and 2-alcohols using a cobalt(II) complex,⁴ but no styrene oxide was observed. Cobalt salen complexes were reported to show catalytic activity for epoxidation of styrene with O₂, but a sacrificial co-reductant, isobutyraldehyde, was necessary.⁵ Recently, CoCl₂ was investigated for the oxidation of monoterpenes with O₂, and it was found that the allylic oxidation proceeded dominantly.⁶ Several heterogeneous cobalt catalysts have been applied for the selective oxidation of alkanes, especially cyclohexane,^{7–11} but very few contribute to the development of heterogeneous catalysts for epoxidation of alkenes with O₂.^{12,13} Recently, we found that Co²⁺-exchanged molecular sieves could catalyze the epoxidation of alkenes with O₂ in the absence of a co-reductant. Here, we report, for the first time, the catalytic performances of the Co²⁺-exchanged faujasite zeolites for the epoxidation of styrene with O₂.

All the parent zeolites used in this work were prepared *via* hydrothermal synthesis and their structures were confirmed by XRD. Cobalt ions were introduced into the zeolites by ion-exchange in aqueous solution of Co(NO₃)₂ for 24 h at temperatures from 298 to 373 K depending on the zeolites. After filtration, and thorough washing with deionized water, the samples were dried at 313 K *in vacuo* for 24 h, and the dried powders were used as catalysts, unless otherwise stated. The cobalt content in each sample was determined by atomic absorption spectroscopic analysis. The epoxidation of styrene was carried out using a batch-type reactor operated under atmospheric pressure. In a typical reaction, a measured amount of catalyst was added to a glass flask pre-charged with the reactant (styrene) and the solvent, typically *N,N*-dimethylformamide (DMF). The reaction was started by bubbling O₂ into the liquid. After reaction for 4 h, the catalyst was filtered off, and the liquid organic products were quantified by a gas chromatograph with a capillary column, using toluene as an internal standard.

The catalytic performances of the Co²⁺-exchanged X zeolite samples with different cobalt contents are shown in Fig. 1. In these experiments, the catalyst weight was kept at 0.2 g. Styrene oxide and benzaldehyde were the two main products along with minor quantities of styrene glycol, benzoic acid and mandelic acid. NaX zeolite without cobalt was almost inactive for the oxidation of styrene, strongly suggesting that cobalt was responsible for the

epoxidation of styrene with O₂. Styrene conversion increased proportionally with an increase in the cobalt content in the sample, while styrene oxide selectivity and the turnover number remained almost the same simultaneously. This result further suggests that the cobalt in the zeolite functions as active sites for the epoxidation of styrene with O₂.

The catalytic properties of various Co-containing samples for the oxidation of styrene with O₂ are compared in Table 1. The weight of catalyst used was regulated in each run to keep the Co amount the same (0.299 mmol). It should be noted that Co²⁺ ions in the liquid phase added as either Co(NO₃)₂ or Co(Ac)₂ were inactive for the epoxidation of styrene. The CoO_x/SiO₂ and CoO_x/NaX samples prepared by the conventional impregnation method could also catalyze the epoxidation of styrene with O₂, but styrene conversion was remarkably lower than for the Co²⁺-exchanged X zeolite. Thus the cobalt ions, which are highly dispersed in the zeolite, played a key role in the catalysis of epoxidation. The comparison among different types of Co²⁺-exchanged zeolites reveals that the Co²⁺-exchanged Y zeolite shows similar catalytic performances to Co²⁺-exchanged X zeolite, and both exhibit much higher styrene conversion than other Co²⁺-exchanged zeolites. Since the window

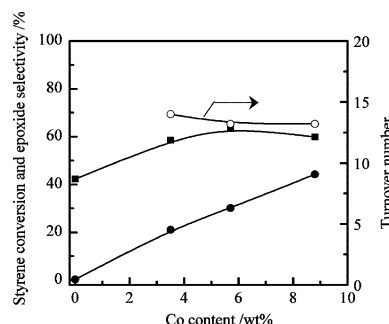


Fig. 1 Catalytic performances of the Co²⁺-exchanged X zeolite samples with different cobalt content: (●) styrene conversion, (■) epoxide selectivity, (○) turnover number. Conditions: *T* = 373 K; styrene, 10 mmol; DMF, 20 ml; flow rate of O₂, 3.0 ml min⁻¹.

Table 1 Catalytic performances of Co-containing samples for the epoxidation of styrene with molecular oxygen

Catalyst	Styrene conv. (%)	Epoxide select. (%)	Turnover no.
NaX	0.32	42.3	–
Co(Ac) ₂	0.40	0	0.12
Co(NO ₃) ₂	0.90	0	0.27
Co ²⁺ -X (8.8 wt%)	44.2	60.0	13.2
Co ²⁺ -X (8.8 wt%) ^a	45.0	65.0	13.4
Co ²⁺ -Y (6.2 wt%)	45.3	62.3	13.5
Co ²⁺ -L (4.3 wt%)	18.2	53.7	4.4
Co ²⁺ -mordenite (2.9 wt%)	15.9	51.7	4.0
Co ²⁺ -beta (1.4 wt%)	25.9	47.6	7.2
CoO _x /SiO ₂ (8.8 wt%)	24.9	60.1	6.8
CoO _x /NaX (8.8 wt%)	30.1	58.9	9.0

Conditions: the amount of Co²⁺ in each catalyst except for NaX, 0.299 mmol; *T* = 373 K; styrene, 10 mmol; DMF, 20 ml; flow rate of O₂, 3.0 ml min⁻¹. ^a Repeated run after three reaction cycles.

size of faujasite zeolites is comparable to that of mordenite and zeolite beta, the particular location of cobalt ions in the faujasite zeolites, or their particular porous structure with supercages may account for their high activity. Several other transition metal ions, such as in Mn²⁺-, Ni²⁺-, Cu²⁺-, Zn²⁺- and Cr³⁺-exchanged X zeolite samples, were also investigated for the epoxidation of styrene with O₂, but styrene conversion and styrene oxide selectivity were both remarkably lower than those for the Co²⁺-exchanged samples. Therefore, the Co²⁺-exchanged faujasite zeolites are unique for the epoxidation of styrene with O₂.

It has been confirmed that no leaching of Co²⁺ from the Co²⁺-exchanged X zeolite occurs during the reaction. The cobalt content in the sample after several reaction cycles did not change, and cobalt could not be detected in the filtrate after the reaction. No significant conversion of styrene was observed when the liquid filtrate was used instead of the solid catalyst for further reaction. Furthermore, the repeated use of the Co²⁺-exchanged X zeolite did not show any decrease in the catalytic activity (Table 1). These observations strongly suggest that the reaction proceeds heterogeneously over the catalyst.

A change in the calcination temperature was found to exert an influence on the catalytic performances for the Co²⁺-exchanged X zeolite samples (Table 2). The sample dried at 313 K *in vacuo* without calcination exhibited the highest styrene conversion. An increase of the calcination temperature gradually decreased styrene conversion and thus the turnover number. It is known that the Co²⁺ ions exchanged in faujasite zeolites may migrate from the supercages to the sodalite cages and further to the hexagonal prisms with an increase in the calcination temperature.¹⁴ Therefore, the results in Table 2 suggest that the Co²⁺ ions located in the supercages of faujasite zeolites are responsible for the epoxidation of styrene with O₂.

Oxygen has been found to be crucial for the epoxidation reaction catalyzed by the Co²⁺-exchanged faujasite zeolites. No reaction occurred without bubbling oxygen to the liquid, and the conversion of styrene increased proportionally with the pressure of O₂ (Fig. 2). Hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP) and NaClO have also been applied for the epoxidation of styrene using the Co²⁺-exchanged X zeolite sample. Although epoxide could be obtained, it is of interest that styrene conversion or styrene oxide selectivity with these oxidants were remarkably lower than those with O₂ (Table 3). The rapid decomposition of H₂O₂ over the catalyst may be responsible for the lower activity and selectivity with H₂O₂. On the other hand, TS-1, a well-known epoxidation catalyst, showed higher activity and selectivity for the epoxidation of styrene with H₂O₂ but almost no activity with O₂.¹⁵ Therefore, oxygen species derived from the activation of O₂ by the Co²⁺ sites in the supercages probably account for the epoxidation of styrene. Further investigations have revealed that the solvent is also important for the epoxidation reactions. It is found that the solvents with higher polarity such as DMF and *N,N*-dimethylacetamide show higher conversion of styrene while those with lower polarity

Table 2 Influence of the calcination temperature on the catalytic performance of the Co²⁺-X (8.8 wt%) sample for the epoxidation of styrene with molecular oxygen^a

Temp./K	Styrene conv. (%)	Epoxide select. (%)	Turnover no.
313	44.2	60.0	13.2
393	37.2	55.5	10.8
573	35.4	62.5	10.4
673	31.4	61.1	9.2
823	25.8	68.4	7.2

^a Conditions are the same with those in Table 1.

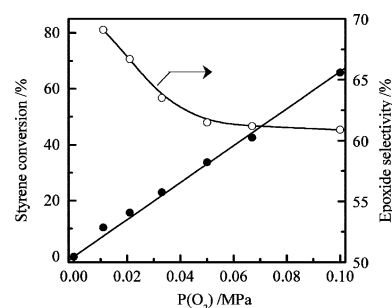


Fig. 2 Effect of O₂ pressure on catalytic performances of the Co²⁺-X (8.8 wt%) sample for the epoxidation of styrene: (●) styrene conversion, (○) epoxide selectivity. Conditions: T = 373 K; styrene, 10 mmol; DMF, 20 ml; total flow rate, 6.0 ml min⁻¹ (O₂ was diluted with N₂).

Table 3 Comparison of different oxidants for the epoxidation of styrene using the Co²⁺-X (8.8 wt%) sample

Oxidant	Styrene conv. (%)	Epoxide select. (%)	Turnover no.
O ₂ ^a	44.2	60.0	13.2
H ₂ O ₂ ^b	20.6	55.5	6.2
TBHP ^c	73.9	12.2	24.8
NaClO ^d	2.6	27.1	0.87

^a Reaction conditions are the same with those in Table 1. ^b Adding 9.7 mmol H₂O₂ instead of bubbling O₂. ^c Adding 10 mmol TBHP instead of bubbling O₂. ^d Adding 10 mmol NaClO instead of bubbling O₂.

such as chlorobenzene give much lower conversion. The nature of the role of solvent and the oxygen species are under investigation.

In conclusion, we have found that the Co²⁺ ions exchanged in faujasite zeolites show unique heterogeneous catalytic properties in the epoxidation of styrene with O₂ in the absence of sacrificial reductant.

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Notes and references

- R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic, New York, 1981.
- J. D. Koola and J. K. Kochi, *J. Org. Chem.*, 1987, **52**, 4545.
- J. E. Lyons, *ACS Adv. Chem. Ser.*, 1974, **132**, 64.
- A. Zombeck, D. E. Hamilton and R. S. Drago, *J. Am. Chem. Soc.*, 1982, **104**, 6782; D. E. Hamilton, R. S. Drago and A. Zombeck, *J. Am. Chem. Soc.*, 1987, **109**, 374.
- B. Rhodes, S. Rowling, P. Tidswell, S. Woodward and S. M. Brown, *J. Mol. Catal. A*, 1997, **116**, 375.
- M. J. da Silva, P. Robles-Dutenhefner, L. Menini and E. V. Gusevskaya, *J. Mol. Catal. A*, 2003, **201**, 71.
- G. Sankar, R. Raja and J. M. Thomas, *Catal. Lett.*, 1998, **55**, 15.
- J. M. Thomas, R. Raja, G. Sankar and R. G. Bell, *Nature*, 1999, **398**, 227.
- I. Belkhir, A. Germain, F. Fajula and E. Fache, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 1761.
- A. F. Masters, J. K. Beattie and A. L. Roa, *Catal. Lett.*, 2001, **75**, 159.
- J. M. Thomas and R. Raja, *Chem. Commun.*, 2001, 675.
- J. M. Thomas, *Angew. Chem., Int. Ed.*, 1999, **38**, 3588.
- D. Dhar, Y. Koltypin, A. Gedanken and S. Chandrasekaran, *Catal. Lett.*, 2003, **86**, 197.
- H. Praliud and G. Coudurier, *J. Chem. Soc. Faraday Trans. I*, 1979, **75**, 2601.
- V. R. Choudhary, N. S. Patil and S. K. Bhargava, *Catal. Lett.*, 2003, **89**, 55.