Simple Metal Oxides as Efficient Heterogeneous Catalysts for Epoxidation of Alkenes by Molecular Oxygen

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Magnetite iron oxide (Fe_3O_4) has been found to be an efficient heterogeneous catalyst for the epoxidation of alkenes by molecular oxygen in the absence of a sacrificial reductant among various transition metal oxides. The reaction probably proceeds via a radical mechanism.

The epoxidation of alkenes is of highly importance because epoxides are versatile synthetic intermediates in chemical industry. Currently, epoxidation is mainly carried out with organic peracid as an oxidant or by a chlorohydrin process, and a large amount of byproducts is formed in either case.[1] Although hydrogen peroxide is an environmentally benign oxidant and several heterogeneous catalysts such as TS-1 have been developed for the epoxidation with H_2O_2,[2] there are still high incentives to exploit molecular oxygen for the epoxidation of alkenes from the environmental, safe and economic considerations. However, only very few successes have been achieved with O_2 as the oxidant except for the epoxidation of ethylene. Although the autooxidation of alkanes such as cyclohexane with O_2 in the presence of transition metal compounds such as cobalt acetate provided useful oxygenated products, the autooxidation of alkenes with the first-row transition metal compounds typically produced a high degree of oxidized polymers as well as cleaved products rather than epoxides.[3] Some transition metal salts and complexes and even scattering heterogeneous catalysts were reported to show activity in the epoxidation reactions with O_2, but in most cases, a co-reductant was indispensable.[4,5] Several homogeneous catalysts such as ruthenium complexes, ruthenium- and iron-substituted polyoxometalates can utilize O_2 for the epoxidation of alkenes without need of the co-reductant,[6] but very scarce heterogeneous catalysts are known.[7] Recently, we found that a very simple and cheap iron oxide, Fe_3O_4, could function as an efficient epoxidation catalyst using O_2 alone. In this communication, we report the superior catalytic performances of Fe_3O_4 for the epoxidation of unfunctionalized alkenes.

The epoxidation of styrene was performed using a batch-type reactor operated under atmospheric pressure. Typically, *N,N*-dimethylformamide (DMF) was used as a solvent, and O_2 was bubbling into the liquid mixture containing styrene and the solvent. For the epoxidation of other alkenes, the reaction mixture was loaded into a Teflon bottle placed in a stainless-steel, high pressure catalytic reactor. O_2 is pressured into the reactor and typically the reaction was allowed to proceed for 4–24 h. After each reaction, the catalyst was filtered off, and the liquid organic products were quantified by a gas chromatograph using toluene as an internal standard.

Figure 1 shows the catalytic performances of various transition metal oxides in the epoxidation of styrene by O_2. Without catalyst, almost no conversion of styrene was observed. As shown in Figure 1, many transition metal oxides could catalyze the epoxidation of styrene with O_2, forming styrene oxide as the main product and benzaldehyde as the main byproduct. Among the transition metal oxides examined, Fe_3O_4 exhibited the highest styrene conversion. Styrene oxide selectivity was also the highest over Fe_3O_4.
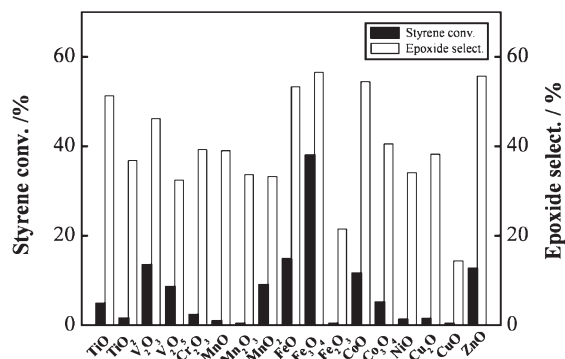

Figure 1. Catalytic performances of various transition metal oxides in the epoxidation of styrene with O_2. Reaction conditions: catalyst, 2.8 mg; temperature, 373 K; styrene, 10 mmol; DMF, 20 mL; flow rate of O_2, 3 mL min^{-1}; reaction time, 4 h.

It is of significance to note that three iron oxides, i.e., FeO, Fe_3O_4, and Fe_2O_3, show different catalytic performances. Further comparisons of these samples are shown in Table 1. FeO and Fe_3O_4 exhibited similar styrene oxide selectivity, but styrene conversion and turnover frequency (TOF, moles of alkene converted per mole of Fe per hour) over FeO were lower than those over Fe_3O_4. The lower activity of FeO may result from its lower specific surface area (< 0.1 m^2 g^{-1}). On the other hand, hematite, Fe_2O_3, possessing similar specific surface area with Fe_3O_4, was almost inactive for the reaction. It is thus reasonable to speculate that the Fe^{2+} existing in the crystalline structure of

Table 1. Epoxidation of styrene with O_2 catalyzed by iron-containing compounds[a]

Entry No.	Catalyst	Surface Area /m^2 g^{-1}	Styrene Conv. /%	Epoxide Select. /%	TOF /h^{-1}
1	FeO	<0.1	14.8	53.3	9.5
2	Fe_3O_4	4.7	38.0	56.5	26.3
3	Fe_2O_3	3.5	0.4	21.5	0.3
4[b]	Fe^{2+}	—	0.3	0	0.05
5[b]	Fe^{3+}	—	0.7	0	0.1

[a]Reaction conditions are the same as in Figure 1. [b]Fe^{2+} and Fe^{3+} were added by dissolving $FeSO_4$ and $Fe_2(SO_4)_3$ (0.2 mmol) into the solvent and the reactant mixture.

Fe_3O_4 or FeO may contribute to its considerably higher activity in the epoxidation of styrene by O_2 with respect to Fe_2O_3. The homogeneous catalytic reaction by dissolving $FeSO_4$ or $Fe_2(SO_4)_3$ in the solvent (DMF) provided only very small amount of benzaldehyde and no formation of styrene oxide was observed. Thus, the epoxidation reaction observed over Fe_3O_4 is heterogeneous in nature.

The influences of O_2 partial pressure on catalytic performances have been investigated under atmospheric pressure by diluting O_2 with N_2. As shown in Figure 2, no reaction took place using pure N_2 or pure argon ($P(O_2) = 0$) instead of O_2. Styrene conversion increased with O_2 pressure from 0 to 0.1 MPa, following a Langmuir-type curve. Simultaneously, styrene oxide selectivity slightly decreased, indicating some consecutive oxidation of styrene oxide to benzaldehyde. Therefore, O_2 played key roles in the epoxidation reaction over Fe_3O_4. We speculate that oxygen is chemisorbed and activated by the Fe^{2+} sites on Fe_3O_4 forming active oxygen species for the epoxidation reactions.
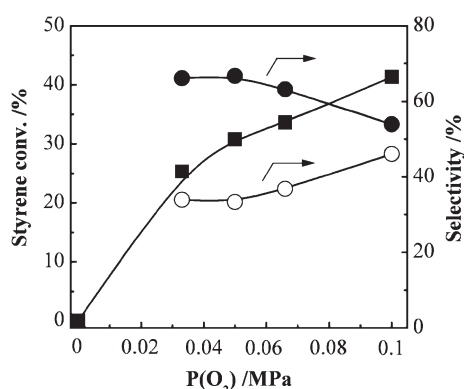
Table 2. Epoxidation of various unfunctionalized alkenes by O_2 over Fe_3O_4[a]

Entry No.	Substrate	Time /h	Alkene Conv. /%	Epoxide Select. /%	TOF /h⁻¹
1		24	69.0	96.7	7.9
2[b]		24	35.4	83.3	2.0
3		8	63.4	75.1	21.8
4[b]		24	51.5	61.9	2.9
5		4	12.1	22.8	8.2

[a]Reaction conditions: Fe_3O_4, 2.8 mg; temperature, 373 K; alkene, 10 mmol; DMF, 20 mL; O_2 pressure, 2 MPa. [b]Alkene, 5 mmol.


Figure 2. Effect of O_2 pressure on catalytic performances for epoxidation of styrene over Fe_3O_4. The other reaction conditions are the same as in Figure 1. (●) styrene oxide, (○) benzaldehyde.

Fe_3O_4 has also been utilized for the epoxidations of other alkenes with higher pressure of O_2 because of their lower activities in atmospheric pressure reactions, and the results are shown in Table 2. It can be seen that the epoxidation of cyclooctene proceeds with high selectivity (>95%), while no reaction occurs without the catalyst under the same reaction conditions. The epoxidations of *trans*-stilbene, 1,1-diphenylstyrene and *trans-β*-methylstyrene with O_2 also resulted in reasonably high selectivity to epoxides over Fe_3O_4. It should be noted that only *trans*-epoxides were obtained in the epoxidations of *trans*-stilbene and *trans-β*-methylstyrene.

It has been verified that no change in catalytic performances in the recycling use of Fe_3O_4 in the epoxidation of styrene by O_2. No change in the crystalline structure of Fe_3O_4 (spinal structure, $Fe^{II}Fe^{III}_2O_4$) was observed after the reaction from the XRD measurements. Thus, Fe_3O_4 is a very stable heterogeneous catalyst for the epoxidation reactions.

The influences of the addition of a radical scavenger, *tert*-butylated hydroxy toluene (BHT), on catalytic performances for epoxidation of styrene over Fe_3O_4 have been investigated. Styrene conversion decreased to almost zero after the addition of ca. 10 μmol BHT to the reactant, suggesting that the reaction may proceed through a radical mechanism. Further details on the mechanism are still under investigations.

References
1 K. Wedissermel and H. J. Arpe, "Industrielle Organische Chemie," Tokyo Kagakudouninn, Tokyo (1996).
2 a) A. Corma and H. Garcia, *Chem. Rev.*, **102**, 3837 (2002). b) I. W. C. E. Arends and R. A. Sheldon, *Top. Catal.*, **19**, 133 (2002). c) G. Grigoropoulou, J. H. Clark, and J. A. Elings, *Green Chem.*, **5**, 1 (2003).
3 a) R. A. Sheldon and J. K. Kochi, "Metal-Catalyzed Oxidation of Organic Compounds," Academic Press, New York (1981). b) J. E. Lyons, *ACS Adv. Chem. Ser.*, **132**, 64 (1974).
4 a) B. Meunier, *Chem. Rev.*, **92**, 1411 (1992). b) C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, **143**, 407 (1995). c) I. Yamanaka, K. Nakagaki, and K. Otsuka, *J. Chem. Soc., Chem. Commun.*, **1995**, 1185. d) B. Rhodes, S. Roeling, P. Tidswell, S. Woodward, and S. M. Brown, *J. Mol. Catal. A: Chem.*, **116**, 375 (1997). e) R. I. Kureshy, N. H. Khan, S. H. R. Abdi, A. K. Bhatt, and P. Iyer, *J. Mol. Catal. A: Chem.*, **121**, 25 (1997). f) T. Punniyamurthy, B. Bhatia, M. M. Reddy, G. C. Maikap, and J. Iqbal, *Tetrahedron*, **53**, 7649 (1997).
5 a) T. Yamada, T. Takai, O. Rhode, and T. Mukaiyama, *Chem. Lett.*, **1991**, 1. b) R. Raja, G. Sankar, and J. M. Thomas, *Chem. Commun.*, **1999**, 829. c) D. Dhar, Y. Koltypin, A. Gedanken, and S. Chandrasekaran, *Catal. Lett.*, **86**, 197 (2003).
6 a) R. A. Budnik and J. K. Kochi, *J. Org. Chem.*, **41**, 1384 (1976). b) J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, **107**, 5790 (1985). c) A. S. Goldstein, R. H. Beer, and R. S. Drago, *J. Am. Chem. Soc.*, **116**, 2424 (1994). d) R. Neumann and M. Dahan, *Nature*, **388**, 353 (1997). e) Y. Nishiyama, Y. Nakagawa, and N. Mizuno, *Angew. Chem., Int. Ed.*, **40**, 3639 (2001).
7 Q. Tang, Y. Wang, J. Liang, P. Wang, Q. Zhang, and H. Wan, *Chem. Commun.*, **2004**, 440.