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Journal of Catalysis 230 (2005) 384–397
JOURNAL OF CATALYSIS
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# Epoxidation of styrene with molecular oxygen catalyzed by cobalt(II)-containing molecular sieves

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Received 11 September 2004; revised 15 December 2004; accepted 16 December 2004

## Abstract

Co-containing molecular sieves, mainly Co–faujasite zeolite and Co-MCM-41, have been studied for the epoxidation of styrene with molecular oxygen. Characterizations with XRD, TEM, laser-Raman, XPS, and $H_2$-TPR suggest that the cobalt introduced into MCM-41 by a template-ion exchange method resembles that exchanged in the faujasite zeolite and exists in the single-site Co(II) state, whereas the sample prepared by the impregnation method contains a large proportion of $Co_3O_4$. The Co(II) sites located in the molecular sieves catalyze the epoxidation of styrene by oxygen with higher activity than $Co_3O_4$ (ca. 2.6 times based on the same cobalt amount). On the other hand, in homogeneous reactions, $Co(NO_3)_2$ and $Co(Ac)_2$ are almost inactive for the conversion of styrene with oxygen, whereas $CoCl_2$ and $Co(acac)_3$ show some activity, but the selectivity for epoxide is remarkably lower as compared with the Co(II)-containing molecular sieves. Among various oxidants examined, oxygen is found to be the best one for the epoxidation of styrene over the Co(II)-containing molecular sieve catalysts. The solvent plays an important role in epoxidation, and superior catalytic performances have been obtained with an acylamide such as *N*,*N*-dimethylformamide (DMF) as the solvent. The oxygen species with a radical nature generated by the activation of molecular oxygen over the solvent-coordinated Co(II) site has been proposed for the epoxidation reactions.

*Keywords:* Epoxidation; Styrene; Molecular oxygen; Cobalt(II)-containing molecular sieves; Faujasite zeolites; MCM-41

## 1. Introduction

The development of effective catalysts for the epoxidation of alkenes to epoxides, which are among the most useful synthetic intermediates, is an important but difficult task in catalysis. Several methods have been developed for the production of epoxides in industry. In the “chlorohydrin” process, epoxides are produced by the intramolecular etherification of chlorohydrins formed by the reaction of alkenes with hypochlorous acid. In the Halcon-Acro and Sumitomo processes, alkyl hydroperoxides are used as oxidants for epoxidation [1]. Although recycling of the co-product (alcohol) has been realized in the Sumitomo process, the need for treatment of large amounts of by-products in these processes has led to the search for other environmentally benign methods, and many intriguing systems have been reported for the epoxidation of alkenes with $H_2O_2$ [1–7], $O_2$ combined with a sacrificial reductant, e.g., $O_2$–$H_2$ [8–13], $O_2$–Zn powder [14] or an $O_2$–organic reductant such as alcohol or aldehyde [15–19], and recently $N_2O$ [20–22] over suitable catalysts. Because of environmental, safety, and economic concerns, however, the utilization of $O_2$ alone for a catalytic epoxidation is most desirable.

So far, only very few studies have achieved epoxidation by $O_2$ in the absence of a sacrificial co-reductant. Two ruthenium complexes, Ru(VI)(TMP)$(O)_2$ (where TMP is tetramesitylporphyrin) and *cis*-$[Ru(dmp)_2(S)_2](PF_6)_2$ (where S $=$ $H_2O$, $CH_3CN$ and dmp is 2,9-dimethyl-1,10-phenanthroline), were reported to catalyze the aerobic epoxidation of alkenes without the need for a co-reductant [23,24]. Recently, ruthenium- and iron-substituted polyoxometalates were

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doi:10.1016/j.jcat.2004.12.017

shown to exhibit good catalytic performance in the epoxidation of alkenes by $O_2$ alone [25,26].

Cobalt ions and complexes are known to catalyze the selective oxidation of alkanes and alkylbenzenes efficiently to organic oxygenates by $O_2$ [27]. On the other hand, oxidation of alkenes with $O_2$, catalyzed by cobalt or other transition metals or transition-metal compounds, generally leads to allylic oxidation products in the first step and consequently produces a high degree of oxidized polymers and cleaved products via autooxidation [27,28]. Budnik and Kochi [29] once reported epoxide formation during the oxidation of *tert*-butylethylene, norbornylene, and 1,1-dineopentylethylene, with $O_2$ catalyzed by Co(III) acetylacetonate (acac), the allylic oxidation of which was difficult to achieve. Reetz and Töllner showed that $Co(acac)_3$ catalyzed the oxidation of styrene only to benzoic acid and benzaldehyde with $O_2$ at 343 K in THF [30]. Cobalt(II) complexes exhibited high reactivity for the epoxidation of various alkenes by *tert*-butyl hydroperoxide (TBHP) and iodosylbenzene [31,32]. Cobalt salen-type complexes were reported to show catalytic activity for the epoxidation of alkenes by $O_2$, but a sacrificial reductant was necessary [33].

As for heterogeneous catalysis, many transition metal-based, especially cobalt-based, catalysts have been studied for the selective oxidation of alkanes such as cyclohexane [34–37], but only very few studies contribute to the epoxidation of alkenes by $O_2$. Raja et al. [38] developed a MAlPO-36 (M = Co or Mn) catalyst effective for the epoxidation of cyclohexene and other alkenes in the presence of an excess of sacrificial aldehyde, based on the work of Yamada et al. [39], who used a homogeneous Ni(II) complex as the catalyst. It is argued that the sacrificial aldehyde is converted to the corresponding peroxy radical, and then the radical induces a specific free radical-based epoxidation [38]. A $CoO_x$-MCM-41 prepared by ultrasonic deposition–precipitation of cobalt tricarbonyl nitrosyl in decalin was once reported to catalyze the epoxidation of alkenes by $O_2$ in the presence of an excess of isobutyraldehyde, which functioned as the sacrificial reductant [40]. Recently, Pruss et al. [41] reported that several cobalt complexes immobilized on HMS modified by organic amines could catalyze the epoxidation of alkenes with $O_2$ and gave moderate selectivity for epoxides in the epoxidation of styrene.

Recently we found and communicated that $Co^{2+}$-exchanged faujasite zeolites could efficiently catalyze the epoxidation of styrene with $O_2$ [42]. Our subsequent investigations showed that Co-MCM-41 prepared by a template-ion exchange method was also effective in the same reaction and even exhibited a higher turnover number at lower cobalt content. In the present paper, we report in detail the characterization and the catalysis of these cobalt-containing molecular sieves in the epoxidation of styrene with $O_2$.

## 2. Experimental

### 2.1. Materials

Parent faujasite zeolites, including NaX with a Si/Al ratio of 1.3 and NaY with a Si/Al ratio of 2.8, were prepared via hydrothermal synthesis with $NaSiO_3 \cdot 9H_2O$, $NaAlO_2$, NaOH, and $H_2O$ as starting materials. The molar ratios of $Na_2O$:$Al_2O_3$:$SiO_2$:$H_2O$ in the synthesis mixtures were 4.8:1:3.7:180 and 8:1:10:160 for the syntheses of NaX and NaY, respectively. After hydrothermal synthesis, the NaX or NaY was washed with deionized water, dried at 313 K in vacuum, and calcined at 823 K in air for 6 h. Cobalt or another transition metal ion was introduced into the faujasite zeolite by ion exchange at room temperature in an aqueous solution of metal nitrate for 24 h. The concentration of the aqueous solution was regulated to control the degree of ion exchange and the cobalt or other transition metal content in the sample [43]. After filtration, washing thoroughly with deionized water, and drying at 313 K in vacuum for 24 h, the sample prepared by the ion-exchange method (denoted as $Co^{2+}$–NaX or $Co^{2+}$–NaY) was obtained.

Cobalt was introduced into MCM-41 by a template-ion exchange (TIE) method. This method is based on the idea that the cationic surfactants in the as-synthesized $S^+I^-$ type of mesoporous materials typified by MCM-41 can be partially replaced through ion exchange by other inorganic cations. Metal (M) ions such as $Mn^{2+}$ [44–46], $VO^{2+}$ [47–49], $Fe^{3+}$ [50,51], and $Cr^{3+}$ [52] have been introduced into MCM-41 with the TIE method. Since there is no cation-exchanging site in the purely silicious MCM-41 after the calcination to remove the organic surfactant, the introduced hetero-metal component may not exist in the single-site state like a cation in the cation-exchanging site of zeolite. Actually, we found that although the TIE method resulted in highly dispersed vanadyl species [48] or $Mn^{2+}$ [46] on the inner surface of MCM-41, the introduced iron [51] and chromium [52] aggregated to form iron oxide clusters and polychromate species, respectively, after calcination. Therefore, the final state of cobalt introduced by the TIE method requires characterization. In our experiments, MCM-41 was first synthesized by a hydrothermal method by the procedure described previously [48]. Then the as-synthesized (uncalcined) MCM-41 containing ca. 50 wt% template (hexadecyltrimethyl ammonium ion, no $Na^+$ and $Br^-$ remained) was added to an ethanolic solution of cobalt(II) nitrate or other transition metal nitrate and stirred vigorously at 333 K for 6 h for ion exchanging between the cationic template and the $Co^{2+}$ or other transition metal ions. After the ion exchange, the as-synthesized Co-MCM-41 was separated by filtration, followed by repeated washing with deionized water, and drying in vacuum at 313 K for 24 h. The sample was finally calcined at 823 K in air for 6 h to remove the remaining organic template [48]. It should be noted that no carbon or nitrogen remained in the calcined samples.