Selective hydroxylation of benzene to phenol by photocatalysis of molybdenum complexes grafted on mesoporous FSM-16

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Mo complexes with Mo_1–Mo_4 nuclearities were grafted on mesoporous silica FSM-16, and their catalytic performances were studied in the hydroxylation of benzene. A trinuclear Mo oxo complex grafted on FSM-16 exhibits the highest catalytic activity in the hydroxylation of benzene to phenol using hydrogen peroxide as an oxidant under the irradiation of UV-light. The turnover numbers for phenol are over 700 at 300 K.

Keywords: molybdenum, FSM-16, hydroxylation of benzene, phenol, photocatalysis

1. Introduction

Direct hydroxylation of benzene to phenol is a potentially attractive route in industry as an alternative of the cumene process [1]. Several homogeneous and heterogeneous catalytic systems consisting of Fenton's reagent, heteropolymolybdovanadophosphoric acids and supported $Pt/V_2O_5/SiO_2$ have been investigated for the hydroxylation of benzene using H_2O_2 or H_2/O_2 as an oxidant [2]. However, in these previous reports, turnover numbers (TONs) based on metal atoms were still unsatisfactory (below 50), and the decomposition of H_2O_2 to O_2 gas substantially occurred to result in lower hydroxylation efficiency of H_2O_2. As the extension of our previous works on the ship-in-bottle synthesis of metal cluster complexes in micro/mesoporous materials [3], mono- and polynuclear Mo complexes were grafted on mesoporous FSM-16, which were active for olefin metathesis [4]. We have employed the resulting Mo complexes grafted on FSM-16 as catalysts for the oxidation of hydrocarbons. Here we report that the Mo_3 oxo complex grafted on mesoporous FSM-16 shows high TONs in the selective hydroxylation of benzene to phenol using H_2O_2 as an oxidant on irradiation of UV-light.

2. Experimental

Supported Mo_1–Mo_4/FSM-16 catalysts were prepared from corresponding Mo complexes: $MoCl_5$, $Mo_2(OAc)_4$, $[Mo_3O(CCH_3)(OAc)_6(MeOH)_3]Cl$ [5] and $[RhCp^*MoO_4]_4$ ($Cp^* = C_5Me_5$) [6]. The powdered FSM-16 (particle size $= 2$–$5\ \mu m$, surface area $= 970\ m^2\,g^{-1}$, pore size $= 2.7$ nm) [7] was dried under vacuum (10^{-3} Torr, 1 Torr $= 133$ Pa) at 773 K for 16 h. $MoCl_5$ was supported on FSM-16 according to the literature method using the Soxhlet extraction [8], and the resulting $MoCl_5$/FSM-16 was calcined in air at 873 K for 7 h. This catalyst is referred to Mo_1/FSM-16. $Mo_2(OAc)_4$ was supported on FSM-16 by the dry-mixing method [4a], and the resulting $Mo_2(OAc)_4$/FSM-16 sample was evacuated at 473 K for 1 h before use as a Mo_2/FSM-16 catalyst. On the other hand, Mo_3/FSM-16 and Mo_4/FSM-16 catalysts were prepared by the impregnation of FSM-16 with methanol solutions of $[Mo_3O(CCH_3)(OAc)_6(MeOH)_3]Cl$ and $[RhCp^*MoO_4]_4$, respectively, and the impregnated samples were dried under vacuum at 300 K. The loadings of Mo were 0.01 wt% for Mo_1, Mo_2 and Mo_4/FSM-16, and 0.005–5 wt% for Mo_3/FSM-16.

The structural characterization of Mo_3/FSM-16 (5 wt% Mo) was performed by means of IR, TPD/MS and EXAFS [4c]. In the EXAFS analysis of Mo_3/FSM-16, the contributions of Mo–Mo, Mo–CCH_3 and Mo–O(μ-oxo) were similar to those of the precursor Mo_3 complex. However, the contribution of Mo–OAc was decreased, while that of Mo–OSi was increased. These EXAFS results indicate that the triangular structure of the Mo_3 complex is retained, and that the acetate ligands are partially substituted by surface OH groups at the mesopores, thus giving $Mo_3O(CCH_3)(OAc)_x(OSi\equiv)_y$ species. In the TPD/MS experiment coupled with IR, the evolution of CH_3OH and CH_3COOH was observed, which also supports the above surface reaction. XRD showed that the mesoporous structure of FSM-16 was conserved after deposition of the Mo_3 complex. These characterization results suggest that the Mo_3 species is grafted in the mesopores of FSM-16 by the reaction with SiOH groups (figure 1).

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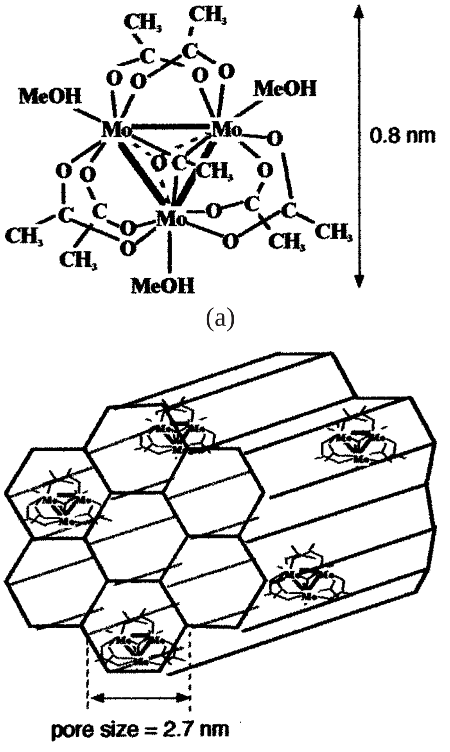


(a)

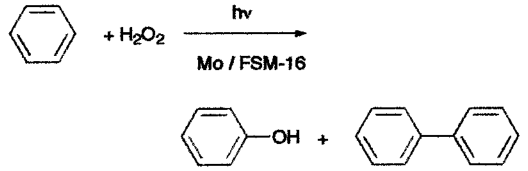
(b)

Figure 1. Mo$_3$ oxo complex $[Mo_3O(CCH_3)(OAc)_6(MeOH)_3]^+$ grafted on FSM-16.

Hydroxylation of benzene was performed in a quartz reactor using a high-pressure mercury lamp (Ushio UM-102, 100 W, $\lambda = 300$–600 nm). Benzene (10 ml, 110 mmol) and aqueous H_2O_2 (diluted to 3.6%, 90 ml, H_2O_2 110 mmol) were added to the catalyst in the reactor, and the mixture was vigorously stirred on irradiation at 300 K. O_2 gas evolved in the reaction was measured using a gas buret connected to the reactor, and was analyzed by GC. A small quantity of reaction mixture (0.5 ml each) was periodically sampled from the reactor, and products were analyzed by GC, HPLC and GC-MS.

3. Results and discussion

Figure 2 summarizes the catalytic performances of the Mo$_1$–Mo$_4$/FSM-16 catalysts (0.01 wt% Mo) for the hydroxylation of benzene on irradiation of UV-light:



(1)

Phenol was formed as a main product of the oxidation of benzene, and the grafted Mo catalysts gave high TONs for phenol: 86–433, where the TONs were calculated based on Mo, i.e., TON = (mol of Ph or Ph–Ph)·(mol of Mo)$^{-1}$. Biphenyl was formed as a minor product, but other by-products such as catechol, quinone and oligomeric oxygenates were not observed under the reaction conditions. Among the Mo$_1$–Mo$_4$/FSM-16 catalysts, Mo$_3$/FSM-16 gave the highest TON for phenol of 433 in 6 h, while the TON for biphenyl was 98. Thus, the ratio of phenol and biphenyl was 82 : 18, which showed a good selectivity for the formation of phenol. To our knowledge, this TON for phenol is remarkably higher than those reported so far (below 50) [2]. Mo$_1$/FSM-16 and Mo$_4$/FSM-16 gave slightly lower TONs for phenol, i.e., 276 and 327, respectively, but Mo$_2$/FSM-16 showed low catalytic activity. When the Mo$_3$ complex itself was used as a homogeneous catalyst, the catalytic activity was significantly low; the TONs for phenol and biphenyl were 3 and 1, respectively. This indicates the promotion effect of grafting Mo$_3$ complex on FSM-16, which may be due to the molecular isolation of the Mo$_3$ complex and the acidity of FSM-16. Moreover, the supported Mo$_3$/FSM-16 catalyst was dispersed in the mixture of benzene and aqueous H_2O_2, which facilitated the biphasic reactions over the catalyst. No leaching of the Mo$_3$ complex from FSM-16 was detected in the UV-vis measurement in the catalytic reactions by Mo$_3$/FSM-16. FSM-16 showed no activity for the hydroxylation of benzene under the same reaction conditions.

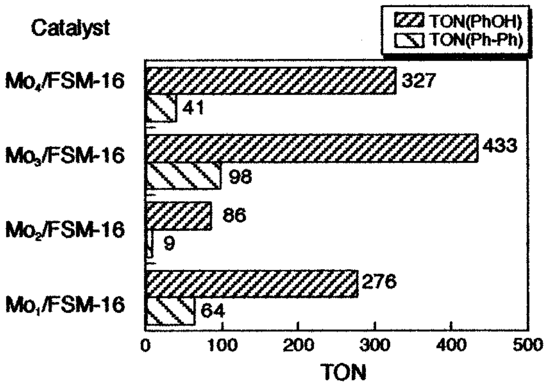


Figure 2. Photooxidation of benzene by Mo complexes grafted on FSM-16. Conditions: catalyst 100 mg (0.01 wt% Mo), benzene 10 ml, aqueous H_2O_2 (3.6%) 90 ml, high-pressure Hg lamp (100 W, 300–600 nm), reaction time 6 h. TON = (mol of PhOH or Ph–Ph)·(mol of Mo)$^{-1}$.

Interestingly, the TON for phenol was increased with decreasing the Mo loading on FSM-16 (figure 3). At the Mo loading of 0.005 wt%, the TON for phenol was increased to 716 in 6 h. Similarly, the phenol : biphenyl ratio was slightly improved to 88 : 12 by increasing the dispersion of Mo$_3$ complex on FSM-16. In the range of Mo loadings below 0.5 wt%, the formation of O_2 from H_2O_2 was not observed, but O_2 was evolved at the loadings over 1 wt%. The enhancement of the TON for phenol and the depression of O_2 evolution at low loadings of Mo may result from the effective site isolation of Mo species on FSM-16.

Figure 4 shows the time-course of TONs for phenol and biphenyl by Mo$_3$/FSM-16 catalyst with or without irradiation of UV-light. Both phenol and biphenyl were linearly formed in the initial reaction time of 4 h on irradiation, but the formation of phenol and biphenyl stopped for another 4 h in the dark. However, it is noteworthy that phenol

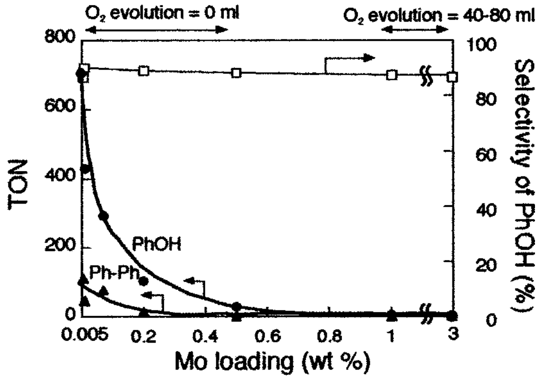


Figure 3. Effect of Mo loading in the photooxidation of benzene. Conditions: catalyst 100 mg, benzene 10 ml, aqueous H_2O_2 (3.6%) 90 ml, high-pressure Hg lamp (100 W, 300–600 nm), reaction time 6 h.

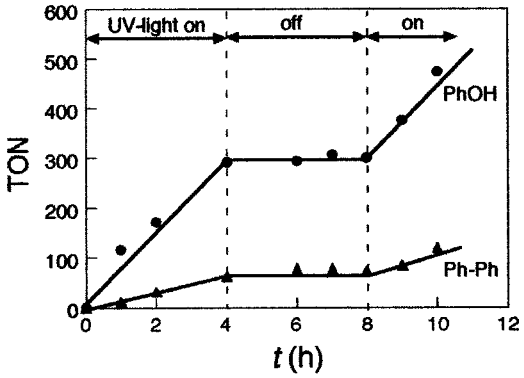


Figure 4. Time-course of TONs for phenol and biphenyl by Mo_3/FSM-16 catalyst with or without irradiation. Conditions: catalyst 100 mg (0.07 wt% Mo/FSM-16), benzene 10 ml, aqueous H_2O_2 (3.6%) 90 ml, high-pressure Hg lamp (100 W, 300–600 nm).

and biphenyl were formed similarly after the irradiation resumed.

The wavelength dependence was studied, and the light of 350–390 nm was effective for the present hydroxylation of benzene over Mo_3/FSM-16. The UV-vis spectrum of $[Mo_3O(CCH_3)(OAc)_6(MeOH)_3]Cl$ in water gave a peak at 380 nm [5]. This peak was decreased by the UV-light in the presence of H_2O_2, and a peak at ca. 510 nm was gradually increased, which was assigned to a bis(μ_3-oxo) complex $[Mo_3O_2(OAc)_6(H_2O)_3]^{2+}$ [9].

From these results, we tentatively propose that the UV-irradiation to the Mo_3 complex leads to removal of the CCH_3 ligand to make a vacant site on the Mo_3 framework on FSM-16, and this species reacts with H_2O_2 to form an OH radical. The OH radical reacts with benzene on the Mo_3 site to form a hydroxycyclohexadienyl radical as in the Fenton-type mechanism [2]. The enhanced activity and selectivity of phenol production on Mo_3/FSM-16 over other Mo_x/FSM-16 may be due to the following reasons: (1) the vacant site on the Mo_3 species efficiently activates H_2O_2 to form an OH radical; (2) this Mo_3 species is less active for the simple decomposition of H_2O_2 to O_2; (3) the Mo_3 site is involved in the oxidation of a hydroxycyclohexadienyl radical to phenol to retard the dimerization to biphenyl. Continuous irradiation is necessary for the photoactivation of the Mo_3 species and/or the regeneration of the vacant site, which enables the catalytic reaction to proceed.

References

[1] R.A. Sheldon and R.A. van Santen, *Catalytic Oxidation: Principles and Applications* (World Scientific, Singapore, 1995);
G. Centi and M. Misono, Catal. Today 41 (1998) 287.

[2] C. Walling and R.A. Johnson, J. Am. Chem. Soc. 97 (1975) 363;
P.T. Tanev, M. Chibwe and T.J. Pinnavaia, Nature 368 (1994) 321;
S. Ito, A. Mitarai, K. Hikino, M. Hirama and K. Sasaki, J. Org. Chem. 57 (1992) 6937;
T. Tagawa, Y. Seo and S. Goto, J. Mol. Catal. 78 (1993) 201;
K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu and Y. Shimizu, J. Mol. Catal. 114 (1996) 181;
X. Lu, N. Mizuno and M. Misono, Nippon Kagaku Kaishi (1998) 23;
T. Miyake, M. Hamada, Y. Sasaki and M. Oguri, Appl. Catal. A 131 (1995) 33;
K. Otsuka, M. Kunieda and H. Yamagata, J. Electrocatal. Soc. 139 (1992) 2381.

[3] M. Ichikawa, in: *Metal Clusters in Chemistry*, eds. P. Braunstein, L.A. Oro and P.R. Raithby (Wiley/VCH, Weinheim, 1999) p. 1273;
M. Ichikawa, in: *Chemisorption and Reactivity on Supported Clusters and Thin Films*, ed. R.M. Lambert (Kluwer, Dordrecht, 1997) p. 153;
M. Ichikawa, Adv. Catal. 38 (1992) 283.

[4] (a) M. Ichikawa, G.J. Li, Q. Zhuang, K. Tanaka and A. Fukuoka, in: *New Frontiers in Catalysis*, ed. L. Guczi (Elsevier, Amsterdam, 1993) p. 529;
(b) Y. Imada, T. Shido, R. Ohnishi and M. Ichikawa, Catal. Lett. 38 (1996) 101;
(c) K. Zama, Y. Imada, A. Fukuoka and M. Ichikawa, Appl. Catal. A 194/195 (2000) 285.

[5] A. Bino, F.A. Cotton, Z. Dori and B.W.S. Kolthammer, J. Am. Chem. Soc. 103 (1981) 5779.

[6] Y. Hayashi, K. Toriumi and K. Isobe, J. Am. Chem. Soc. 110 (1988) 3666.

[7] S. Inagaki, Y. Fukushima and K. Kuroda, J. Chem. Soc. Chem. Commun. (1993) 680.

[8] M. Anpo, M. Kondo, S. Coluccia, C. Louis and M. Che, J. Am. Chem. Soc. 111 (1989) 8791.

[9] M. Ardon, A. Bino, F.A. Cotton, Z. Dori, M. Kaftory and G. Reisner, Inorg. Chem. 21 (1982) 1912.