

# Cyclohexane Functionalization Catalyzed by Octahedral Molecular Sieve (OMS-1) Materials

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Both the abundance of alkanes and their extremely low activity have greatly interested several researchers. In this paper, different metal substituted  $3 \times 3$  octahedral molecular sieves (OMS-1) materials were used to catalyze the functionalization of cyclohexane by using tert-butyl hydroperoxide as oxidant and tert-butyl alcohol as solvent at different temperatures (60, 80, and 100°C). [Fe]-OMS-1 at 80°C exhibits the best activity and selectivity. The solvent t-butyl alcohol (the reduced state of t-butyl hydroperoxide) was first introduced to the reaction system which makes the system simple to study. The effects of catalyst amount and ratio of tert-butyl alcohol to cyclohexane were examined. Variable speed stirring (200–800 rpm) experiments suggest that under conditions reported here that diffusion is not a problem. Studies of the liquid phase after separation from the solid OMS-1 catalysts have shown that metal does not leach into the solution and that heterogeneous catalysis occurs. At 80°C, the conversion of cyclohexane or the total yield of products can reach 13.1% in 40 h. The yields of cyclohexanone, cyclohexanol, and cyclohexyl hydroperoxide were 6.57, 2.83, and 1.38%, respectively, and t-butyl cyclohexyl perether was 2.36%. The reaction conditions are mild, and the catalysts retain their crystallinity after reaction. Moreover, the catalyst can be easily separated from the reaction mixture and used catalysts retain similar catalytic activity over a 40-h time period. © 1998 Academic Press

## 1. INTRODUCTION

The abundance of saturated hydrocarbons has led to the interest of several researchers since the early 1980s to try to activate these materials (1–3). However, their very low reactivity poses a severe challenge toward exploration and potential commercial use. A lot of work involving organometallic complexes that imitate the activity of enzymes such as cytochrome p-450 monooxygenase has been done (4–9). Usually dioxygen is unable to oxidize these inert hydrocarbons even in the presence of active organometallic complex catalysts (10–14). Photochemical reactions with UV radiation catalyzed by  $\text{TiO}_2/\text{TS-1}$  (15), by metal-porphyrin complexes (16) or by porphyrin modi-

fied  $\text{TiO}_2$  (17, 18) show good oxidation results, but with the formation of significant amounts of  $\text{CO}_x$  (15–18).

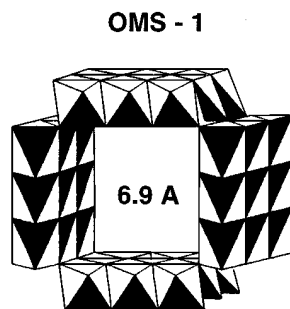
Hydrogen peroxide and tert-butyl hydroperoxide (TBHP) have been used widely for selective oxidation. Systems based on functionalization of cyclohexane via oxidation with  $\text{H}_2\text{O}_2$  catalyzed by organometallic complexes have attained high conversions and selectivities (10, 19–24). Fewer reports have been published using heterogeneous catalysts. Titanium silicate (25, 26), vanadium silicate (27), chromium silicate (28), and  $\text{Mn}^{2+}$ -exchanged clay (29), as well as vanadium-substituted MCM-41 zeolite (30), were employed as catalysts and all these systems show interesting oxidation reactions. However, the presence of large amounts of water usually culminates in a two-phase system with inherent separation problems. Moreover, metal (Ti, V, and Cr) silicates show good activities for the oxidation of linear alkanes (25, 31–33), but much lower activities for the oxidation of cycloalkanes, like cyclohexane (33, 34).

We have used TBHP (70% aqueous solution) as the oxidant, with t-butyl alcohol (TBA) as the solvent to avoid phase separation problems. TBA is also the decomposition product of TBHP, so that complete miscibility of the reaction mixture can be ensured. Several papers were published (1, 28, 30, 33–37) with TBHP as the oxidant, but mostly using complicated organometallic complexes as catalysts. In pursuing our interest in the catalytic behavior of manganese oxides, we have used manganese oxide catalysts that have the todorokite structure (hereafter designated as OMS-1 (38, 39); see Fig. 1).

Octahedral molecular sieves used in this research are microporous tunnel-structure materials. They are mixed valent systems that are good semiconductors. These synthetic materials have been modeled after natural manganese nodules. The synthetic versions are much purer than natural materials and can be systematically doped with various transition metals in the framework of  $\text{MnO}_6$  octahedra. Exchangeable cations in the tunnels of these materials can be replaced via ion-exchange methods.

OMS-1 possesses a  $3 \times 3$  tunnel structure with a tunnel opening of about 6.9 Å. The basic building blocks of this

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**FIG. 1.** Structure of OMS-1, synthetic todorokite,  $\text{Mg}_{0.98-1.35}^{2+} \text{Mn}_{1.89-1.94}^{2+} \text{Mn}_{4.38-4.54}^{4+} \text{O}_{12} \cdot 4.47 - 4.55 \text{H}_2\text{O}$ .

material are  $\text{MnO}_6$  octahedra that are interconnected by edges and corners. When doped with a lower valent transition metal, these transition metal cations ( $\text{M}^{2+/3+}$ ) can replace Mn cations in the framework to form  $\text{MO}_6$  units or ions that can occupy tunnel positions. Catalytic studies of OMS-1 and metal doped OMS-1 materials in the functionalization of cyclohexane with TBHP as oxidant are presented here.

## II. EXPERIMENTS

### A. Synthesis of Doped OMS-1 (38, 39)

The preparation of catalysts was done in the following way: a 60 mL volume of a 5.0 M NaOH solution was added dropwise to a vigorously stirred 40 mL mixture of 0.5 M  $\text{MnCl}_2$ , 0.1 M  $\text{MgCl}_2$  to form a suspension in a plastic flask at room temperature. After that, 40 mL of 0.2 M  $\text{KMnO}_4$  solution was added dropwise to a vigorously stirred suspension, and stirring was stopped upon completion of this addition. The plastic flask was sealed and aged at 35°C for 2 days before filtration and the solid powder was washed with distilled deionized water (DDW). The filtered residue was ion-exchanged by using 200 mL of 1.0 M  $\text{MgCl}_2$  overnight at room temperature, and the exchanged material was filtered and washed with DDW. The mixture was transferred to an autoclave at 150°C for 2 days. The final product was filtered and washed, and then dried at 110°C overnight. For the synthesis of framework substituted OMS-1 materials, the only difference is that 8 mL of 0.1 M transition metal salt was added to the mixture of  $\text{MnCl}_2$  and  $\text{MgCl}_2$  (40).

### B. Catalytic Reactions

Stirred reaction mixtures in sealed glass vials were heated at reaction temperatures of 80°C or lower. The reactions at 100°C were done in stirred autoclaves which had Teflon liners. All the reaction vessels were placed in a temperature-controlled oil bath. The reaction mixture is generally composed of: OMS-1, 67 mg; cyclohexane, 1.8 g; TPHP, 2.0 g (70% aqueous solution); t-butyl alcohol, 4.2 g as solvent.

Otherwise the composition of the mixture will be specified. Acetophenone was added as an internal standard. The reaction products were qualitatively analyzed by GC-MS and GC-IR and quantitatively analyzed by GC (HP 5890 series II) with a Supelcowax-10 column.

All the catalysts were sieved to a size of 50 mesh or smaller with crystallite sizes of about 200 Å as determined by transmission electron microscopy.

## III. RESULTS

### A. Effects of Reaction Temperatures for Different Catalysts

The different substituted OMS-1 and commercial  $\text{MnO}_2$  (Chemetals Division, Diamond Shamrock Chemicals) were tested at 60, 80, and 100°C, respectively. Chemical analyses of the OMS-1 materials show that their compositions are:  $\text{Mg}_{1.10}\text{Mn}_{6.41}\text{O}_{12} \cdot 4.31\text{H}_2\text{O}$  (OMS-1);  $\text{Mg}_{1.12}\text{Fe}_{0.20}\text{Mn}_{6.21}\text{O}_{12} \cdot 4.21\text{H}_2\text{O}$  ([Fe]-OMS-1);  $\text{Mg}_{1.21}\text{Co}_{0.24}\text{Mn}_{5.98}\text{O}_{12} \cdot 3.58\text{H}_2\text{O}$  ([Co]-OMS-1);  $\text{Mg}_{1.08}\text{Cu}_{0.21}\text{Mn}_{6.18}\text{O}_{12} \cdot 3.84\text{H}_2\text{O}$  ([Cu]-OMS-1); and  $\text{Mg}_{1.15}\text{Cr}_{0.19}\text{Mn}_{6.25}\text{O}_{12} \cdot 3.66\text{H}_2\text{O}$  ([Cr]-OMS-1).

Table 1 shows results of reaction at 60°C. OMS-1 materials show significant catalytic activity as compared to commercial  $\text{MnO}_2$ . Metal substituted OMS-1 materials have better catalytic activity than OMS-1 itself and [Fe]-OMS-1 has the best activity among the catalysts tested (see Fig. 2). However, cyclohexyl hydroperoxide (CHP) is the main product for all the catalysts at 60°C. The conversion of cyclohexane and the total yield of all products (no other products were detected) decrease in the order [Fe]-OMS-1 > [Co]-OMS-1 > [Cu]-OMS-1 > [Cr]-OMS-1 > OMS-1 >>  $\text{MnO}_2$ .

The data of Table 2 suggest that when the reaction temperature is raised to 80°C that the product distribution changes significantly. The conversion of cyclohexane at 80°C increases considerably as compared to that at 60°C for all catalysts. The yields of cyclohexanol (A) and cyclohexanone (K) increase greatly at the expense of CHP. The yield of t-butyl cyclohexyl perether (P) is more than twice that at 60°C. In addition, the activity order of the catalysts at 80°C is different from that at 60°C. [Cu]- and [Cr]-OMS-1

**TABLE 1**  
Cyclohexane Oxidation at 60°C for 40 h

Type of catalysts	% conversion	% A	% K	% CHP	% P
[Fe]-OMS-1	6.79	1.78	2.45	1.81	0.75
[Co]-OMS-1	4.60	0.99	1.13	2.12	0.36
[Cu]-OMS-1	4.59	0.88	1.15	2.02	0.54
[Cr]-OMS-1	4.42	0.98	1.13	1.99	0.32
OMS-1	3.98	0.84	0.90	1.95	0.29
$\text{MnO}_2$ commercial	0.11	0	0	0.11	0

*Note.* A = cyclohexanol, K = cyclohexanone, CHP = cyclohexyl hydroperoxide, P = t-butyl cyclohexyl perether, catalyst: 67 mg, cyclohexane: 1.8 g, TBHP (70% aqueous solution): 2.0 g, t-butyl alcohol: 4.2 g.

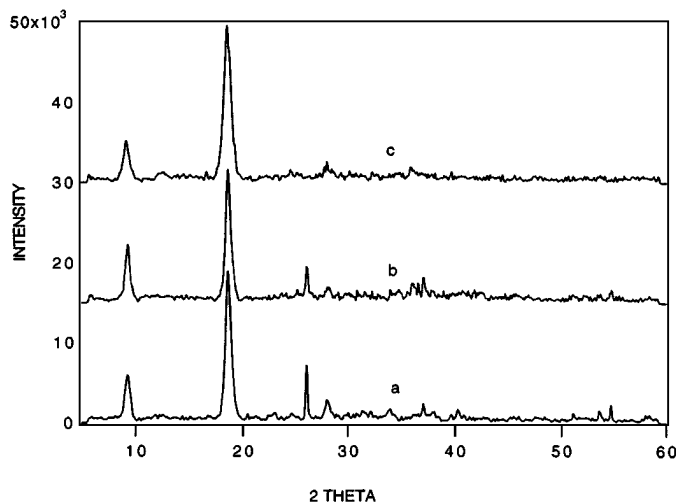


FIG. 2. The XRD patterns of [Fe]-OMS-1: (a) fresh; (b) used catalyst after one run, 40 h; (c) used catalyst after two runs; total time = 80 h.

showed higher activity than [Co]-OMS-1 at 80°C. Commercial MnO<sub>2</sub> shows the least activity with only P formed at 60 and 80°C.

Two things are very obvious for reactions at 100°C (see Table 3): first, no CHP exists in the reaction products after reaction for 40 h; second, all the catalysts (both substituted and unsubstituted OMS-1 materials) have similar activity. Generally, ketone and *t*-butyl cyclohexyl perether occur in higher yields than at lower temperatures, and the ratios of K/A increase along with an increase in reaction temperature. One exception is [Fe]-OMS-1, where the ratio of K/A is smaller at 100°C than that at 80°C. At 60–100°C, cyclohexane conversion and yields of products increase with the increase of reaction temperature, and no deep oxidation products have been detected. However, the increase of conversion or total yields as the reaction temperature increases from 80 to 100°C is rather insignificant as compared to the increase from 60 to 80°C. Therefore, a reaction temperature of 80°C was chosen for further studies.

TABLE 2

Cyclohexane Oxidation at 80°C for 40 h

Type of catalysts	% conversion	% A	% K	% CHP	% P
[Fe]-OMS-1	11.6	3.45	5.54	0.56	2.11
[Co]-OMS-1	9.44	2.95	4.17	1.13	1.09
[Cu]-OMS-1	10.3	3.41	4.59	1.01	1.05
[Cr]-OMS-1	10.2	3.18	4.61	1.11	1.25
OMS-1	9.4	3.03	4.19	1.08	1.08
MnO <sub>2</sub>	1.01	0	0	1.01	0

Note. A = cyclohexanol, K = cyclohexanone, CHP = cyclohexyl hydroperoxide, P = *t*-butyl cyclohexyl perether; catalyst: 67 mg, cyclohexane: 1.8 g, TBHP (70% aqueous solution): 2.0 g, *t*-butyl alcohol: 4.2 g.

TABLE 3

Cyclohexane Oxidation at 100°C for 40 h

Type of catalysts	% conversion	% A	% K	% CHP	% P
[Fe]-OMS-1	15.4	4.61	7.49	0	3.32
[Co]-OMS-1	14.9	4.21	6.83	0	3.83
[Cu]-OMS-1	15.1	4.33	6.85	0	4.84
[Cr]-OMS-1	15.4	4.10	7.01	0	4.28
OMS-1	15.0	4.00	6.92	0	4.12

Note. A = cyclohexanol, K = cyclohexanone, CHP = cyclohexyl hydroperoxide, P = *t*-butyl cyclohexyl perether; catalyst: 67 mg, cyclohexane: 1.8 g, TBHP (70% aqueous solution): 2.0 g, *t*-butyl alcohol: 4.2 g.

### B. Effects of Stirring Speed

The effects of stirring speed were conducted to examine mass transfer effects (41). Stirring speeds from 200 to 800 rpm, as well as no stirring, have been used and the results are listed in Table 4.

Table 4 shows that cyclohexane conversions and yields of different products are different for stirred and nonstirred reactions. There is a big difference in terms of initial reaction rates for stirred and nonstirred experiments, but there is only a small difference for reaction rates with stirring speeds from 200 to 800 rpm. These data suggest that mass transfer effects can be minimized if a stirring speed of 200 rpm or higher is applied. A stirring speed of 400 rpm was generally used to test for effects of the amount of TBHP, the amount of solvent, and other factors in these reactions.

### C. Effects of Amount of Tert-Butyl Hydrogen Peroxide

The original amount of TBHP was 2.0 g (70% aqueous solution) in the reaction mixture. In order to study the effect of the amount of TBHP, all factors and components other than TBHP were kept the same. The amounts of TBHP chosen are 1.0, 2.0, 3.0, and 4.0 g, respectively.

Table 5 shows that cyclohexane conversion is affected by the amount of TBHP. It is clear that yield of every single product increases as the amount of TBHP increases. The efficiency of TBHP decreases as the amount of TBHP increases. An amount of 2.0 g of TBHP was used in the reaction mixture for all of the experiments described below since the cyclohexane conversion showed a large increase when TBHP was changed from 1.0 to 2.0 g.

### D. Effects of Catalyst Amount

Catalyst amounts were changed from 0 to 84 mg for reactions carried out at 80°C. All the results are shown in Table 6. The data of Table 6 demonstrate that the presence of very small amounts of catalyst (4 mg) lead to large increases in cyclohexane conversion. However, cyclohexane conversions and yields of cyclohexanone become flat when 17 mg catalyst are used, although there is a general trend of higher conversion and higher total yields with higher

TABLE 4  
Effects of Stirring Speed for Cyclohexane Oxidation at 80°C for 40 h

Stirring speed	% conversion	Rate $\times 10^4$ <sup>a</sup> (mol · g <sup>-1</sup> · s <sup>-1</sup> )	% A	% K	% CHP	% P	% selectivity of TBHP
0	9.45	0.59	2.38	4.67	0.39	2.01	30.7
200 rpm	11.3	1.93	3.31	5.47	0.58	2.17	32.9
400 rpm	11.6	1.99	3.45	5.54	0.56	2.11	33.5
600 rpm	11.7	2.12	3.34	5.62	0.59	2.15	34.1
800 rpm	11.5	2.03	3.36	5.51	0.54	2.09	33.2

Note. A = cyclohexanol, K = cyclohexanone, CHP = cyclohexyl hydroperoxide, P = t-butyl cyclohexyl perether; catalyst: 67 mg, cyclohexane: 1.8 g, TBHP (70% aqueous solution): 2.0 g, t-butyl alcohol: 4.2 g.

<sup>a</sup> Initial rates of reaction.

catalyst amounts. The yield of cyclohexanol rises to a maximum at 67 mg catalyst, and decreases with further increase of catalyst amount. On the other hand, the yields of cyclohexanol and P increase continually with the increase of catalyst amount. The continuous and rather drastic decrease in CHP formation with the increase of catalyst amount should be noted. CHP disappears when 84 mg catalyst was used.

The normalized initial reaction rates which were obtained from differentiated data of conversions with respect to time are similar, even though the conversions and yields of different products are not similar.

#### E. Effects of Solvent Amount

The weight ratio of TBA to cyclohexane was 2.50 in all previously mentioned experiments and this is the ratio that can ensure complete miscibility of reactants at room temperature. This ratio was varied to study solvent effects over a certain range (1.40–2.50). Table 5 shows that the conversion changes as the amount of solvent changes. The ratio of t-butyl alcohol to cyclohexane of 1.8 is the best for the conversion of cyclohexane and for the yields of total products. As the ratio of tert-butyl alcohol to cyclohexane increases, the yield of CHP goes down, and at the same time, the yield of cyclohexanol and P go up. The conversion of cyclohexane and total yield of oxidation products reach a maximum when the weight ratio of TBA to cyclohexane is 1.8. This

TABLE 5  
Effects of Amount of TBHP on Cyclohexane Oxidation  
at 80°C for 40 h

TBHP (70%) (g)	% conversion	% A	% K	% CHP	% P	% selectivity of TBHP
1.0	9.37	3.63	4.32	0.21	1.21	40.6
2.0	11.6	3.45	5.54	0.56	2.11	33.5
3.0	13.0	3.71	6.34	0.70	2.25	31.4
4.0	13.8	3.74	6.97	0.75	2.34	29.6

Note. A = cyclohexanol, K = cyclohexanone, CHP = cyclohexyl hydroperoxide, P = t-butyl cyclohexyl perether; catalyst: 67 mg; TBA: 4.2 g; cyclohexane: 1.8 g; reaction time: 40 h.

ratio of TBA to cyclohexane was used in all experiments discussed below.

#### F. Effects of Reaction Time

Figure 3 shows that the conversion of cyclohexane at 60°C changes over a 25-h period when 67 mg [Fe]-OMS-1 is used. It appears that the conversion of cyclohexane and total yields of products increase continuously as time increases. Figure 4 shows the change of product distribution with time at 60°C within a 25-h reaction period. The yield of each product increases with reaction time as shown by the changes in slopes of curves of products in Fig. 4. The formation of CHP increases steeply during an initial 6-h period. CHP formation then slows down with further increase of reaction time and seems to level off near a reaction time of 25 h. The formation of alcohol also increases steeply during the initial 6 h, but thereafter it slows down very quickly. At the same time, the concentration of TBHP in the reaction mixture at the end of 25 h of reaction is about 63% of its original value.

Figure 5 shows data for the reaction at 80°C. The conversion of cyclohexane increases dramatically during the first

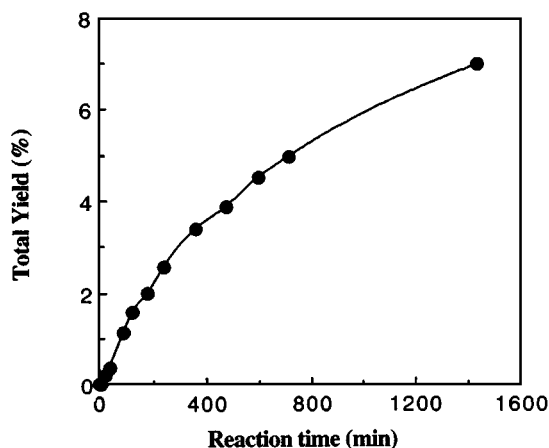


FIG. 3. Conversion of cyclohexane as a function of time at 60°C with [Fe]-OMS-1 catalyst: ●, conversion of cyclohexane.

TABLE 6  
Effects of Catalyst Amount for Cyclohexane Oxidation at 80°C

Catalyst amount (mg)	Rate $\times 10^4$ <sup>a</sup> (mol · g <sup>-1</sup> · s <sup>-1</sup> )	% conversion	% A	% K	% CHP	% P	% selectivity of TBHP
0	0	0	0	0	0	0	—
4	2.23	7.41	1.04	1.25	4.16	0.96	51.4
8	2.15	8.90	1.82	2.79	2.97	1.32	44.7
12	1.93	9.52	2.11	3.64	2.13	1.63	40.2
17	2.32	10.2	2.58	4.24	1.78	1.59	37.3
49	2.12	11.3	3.40	5.31	0.90	1.66	35.7
67	1.99	11.6	3.45	5.54	0.56	2.10	33.1
84	1.86	12.2	3.34	6.20	0	2.64	29.5

Note. A = cyclohexanol, K = cyclohexanone, CHP = cyclohexyl hydroperoxide, P = t-butyl cyclohexyl perether, cyclohexane: 1.8 g; TBHP (70% aqueous solution): 2.0 g; TBA: 4.2 g; reaction time: 40 h.

<sup>a</sup> Normalized initial rate (mole · catalyst<sup>-1</sup> · time<sup>-1</sup>).

10 h; thereafter it levels off quickly to 13.1% conversion at a reaction time of 40 h. This change in conversion versus time is clearly quite different from data for the reaction at 60°C (see Fig. 4). Figure 6 shows the change in product distribution for reactions at 80°C. The initial rates of formation of each product are all faster than at 60°C. For the formation of alcohol, the data at 80°C are similar to those at 60°C. The yield of alcohol keeps growing during the first few hours and it does not increase much after that, and even drops slightly after 25 h. The trend of formation of P at 80°C is not very different from at 60°C. The rate of formation of ketone at 80°C shows a continuous decline in slope with reaction time, and levels off to 7% yield at 25 h. The conversion of cyclohexane is 12.7% at 80°C as compared to 6.9% at 60°C. Considerable amounts of TBHP (35.1%) remained after 25 h of reaction. The rate of formation of CHP at 80°C shows an obvious maximum at a reaction time of 9 h.

### G. The Reusability of Catalysts and Heterogeneity of Reaction

The used [Fe]-OMS-1 materials were filtered, washed with water, dried at 110°C overnight in air, and then used as catalysts. A weight ratio of t-butyl alcohol to cyclohexane of 1.8 was chosen. All the other factors and reaction conditions were the same as described in Section III.F, except for time. The results for used catalysts are shown in the bottom line of Table 6. The conversion of cyclohexane or total yields of product is 12.8% for the used catalyst. The yields of cyclohexanol and cyclohexanone of the used catalyst were slightly higher than that of a new catalyst, but the yields of CHP and P were slightly lower than that of new catalysts. The powder X-ray diffraction (XRD) data were collected for the catalysts (fresh, after one run, after two runs), and all XRD patterns are shown in Fig. 2. It is clear that crystallinity was retained after two runs and that the intensities did not show any obvious change. Crystallinity

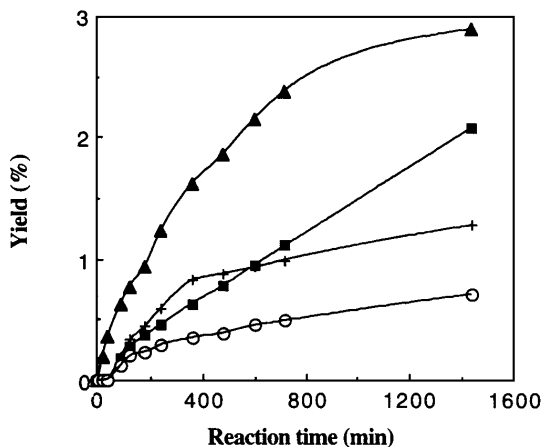


FIG. 4. Yields of products as a function of time at 60°C with [Fe]-OMS-1 as catalyst: ■, cyclohexanone; ✚, cyclohexanol; ○, t-butyl cyclohexyl perether; ▲, cyclohexyl hydroperoxide.

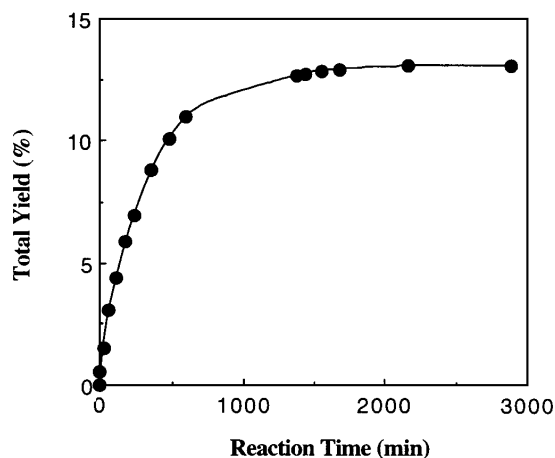


FIG. 5. Conversion of cyclohexane catalyzed with [Fe]-OMS-1 versus time at 80°C: ●, conversion of cyclohexane.

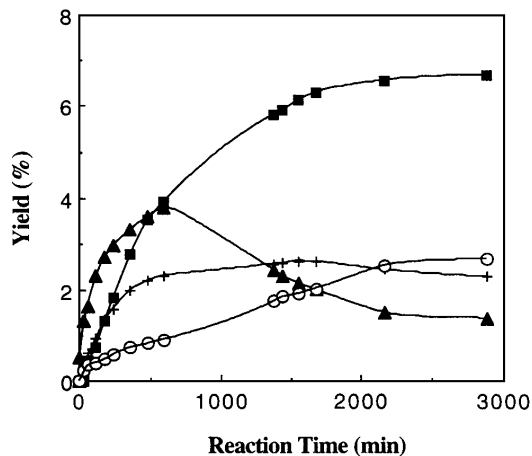


FIG. 6. Yields of products catalyzed with [Fe]-OMS-1 versus time at 80°C: ■, cyclohexanone; +, cyclohexanol; O, t-butyl cyclohexyl perether; ▲, cyclohexyl hydroperoxide.

was retained for all metal doped catalysts after reaction as shown by XRD data.

To study whether the catalytic reaction is heterogeneous or homogeneous, solutions of reaction mixtures after the solid was filtered were further mixed with fresh reactants (cyclohexane and TBHP) and solvent (TBA). No catalyst was added. The mixture was split into two parts. One part was stored at room temperature without stirring, and another was stirred and heated at 80°C for 40 h. Both mixtures were analyzed by GC methods and no reactivity was observed for either part. The filtered solutions were also analyzed by inductively coupled plasma (ICP) analyses. No transition metal ions were detected in solution.

#### IV. DISCUSSION

##### A. Effects of Temperature

Data of Table 1 show that the conversion of cyclohexane and the total yields of oxidation products increase as the reaction temperature is increased. The increases in conversion and yield from 80 to 100°C are smaller than that from 60 to 80°C. This may be because there is a smaller activation energy at higher temperature than that at lower temperature. The ratio of K/A goes up when temperature increases from 60 to 100°C, and this implies that A is continually oxidized at a higher temperature.

These observations are different from the data reported by Menage *et al.* (36) and Leising *et al.* (1). They used TBHP to oxidize cyclohexane and found that the K/A ratio reached almost one when ( $\mu$ -oxo) diferric complexes were used as catalysts. They suggested a mechanism where A, K, and P all form concurrently and are all stable. What they suggested for P seems to be true in our reaction system because the yield of P increases as the temperature is

increased. Data of Figs. 4 and 6 also suggest that P is stable as evidenced by the changing yields with reaction time.

The formation of CHP has not yet been reported in liquid phase reaction systems. The selectivity of CHP decreases as the reaction temperature increases from 60 to 80°C and becomes 0 at 100°C, suggesting that CHP is an unstable intermediate. The fact that CHP has a maximum yield at 9 h, as shown in Fig. 6, clearly indicates that CHP is an unstable intermediate and that it transforms to other stable compounds such as ketones.

The efficiency of TBHP decreases as reaction temperature is increased due to the decomposition of peroxide. The decomposition of peroxide is faster at higher temperature.

##### B. Effects of Stirring Speed

Even though there are differences in terms of conversions and total yields of different products for stirred and nonstirred systems, the largest difference is the initial rate of reaction. The initial reaction rate for the reaction without stirring is less than one-third that with stirring. This indicates that diffusion limitations exist for the reaction without stirring. However, the initial rates for the reaction with stirring speeds of 200 to 800 rpm are more than 3 times greater than the rate for reaction without stirring and only small differences between the reactions with stirring rates of 200 rpm or higher were observed. No obvious diffusion problem exists if the stirring speed is greater than 200 rpm as shown by the small differences in conversions, yields of different products, and selectivities of TBHP. Micropore diffusion is unlikely a problem because the particle sizes are small. To ensure that diffusion problems were eliminated, a stirring rate of about 400 rpm was selected.

##### C. Effects of Amount of Tert-Butyl Hydrogen Peroxide

The conversion of cyclohexane increases as the amount of TBHP used in the reaction increases as shown in Table 5. More TBHP reactant drives the reaction and favors the formation of products. The amounts of P and CHP also increase as TBHP increases. The yields of cyclohexanol and cyclohexanone are similar when 1.0 g of TBHP is added to the reaction system. The ratio of ketone to alcohol increases when more TBHP is present in the reaction mixture. More TBHP causes more deep oxidation and favors the production of ketone and minimizes alcohol formation.

##### D. Effects of Catalyst Amount

The results of the effect of catalyst amount shown in Table 4 demonstrate clearly that [Fe]-OMS-1 is very active in this reaction system, and that even tiny amounts of catalyst (4 mg) can lead to significant conversion. The continuous decrease of CHP formation and formation of more stable products like K and P with increasing catalyst amount show similar trends when reaction temperature is increased. Even though the normalized initial reaction rates

(disappearance of cyclohexane) are very similar for catalyst amounts of 4 to 84 mg (initial rates are proportional to the catalyst amount), the conversions are not similar. The rate of reaction decreased much faster with a large amount of catalyst than with a small amount of catalyst. Analysis of the reaction mixture at various reaction times and at different temperatures is also needed in order to better understand the reaction (see Section III.F). In addition, [Fe]-OMS-1 catalysts may lead to a better understanding of the role of Fe in the natural enzyme cytochrome p-450 which catalyzes the monooxygenation of methane (2).

#### E. Effects of Solvent Amount

The t-butyl alcohol solvent plays a very important role in terms of cyclohexane conversion and product distribution as shown in Table 5. One interesting trend is that as the ratio of tert-butyl alcohol to cyclohexane increases, the yield of CHP decreases. At the same time, the yields of cyclohexanol and P increase. These trends may be due to the reaction equilibrium being favorable for the formation of P and to the decrease of CHP when the amount of t-butyl alcohol increases.

The yield of cyclohexanol increases as the amount of solvent increases, perhaps because as more t-butyl alcohol was added the physical properties (polarity, etc.) of the reaction mixture are more favorable for the formation of cyclohexanol. The decrease in conversion of cyclohexane on increasing the solvent to cyclohexane ratio from 1.8 to 2.5 implies that a lowering of reactant concentration is detrimental for the oxidation reaction. The reason that the conversion of cyclohexane also decreases when the solvent to cyclohexane ratio changes from 1.8 to 1.4 is that less solvent results in incomplete dissolution and makes the reaction more difficult to proceed.

#### F. Effects of Reaction Time

Figure 3 shows that the conversion of cyclohexane increases continuously up to 6.9% after 25 h of reaction. At the same time, 63.0% of the original amount of TBHP is still present. This indicates that the reaction is far from completion. A comparison of Figs. 4 and 6 shows that the trends in formation of K and P (increasing amounts) are similar at 60 and 80°C. However, the changing trends for A and CHP are quite different at these two temperatures. A eventually levels off at 80°C, whereas CHP goes through a maximum at 80°C. At 80°C, cyclohexanol levels off after 9 h and starts to decrease after 30 h. All these data suggest that the alcohol is continually oxidized.

The rate of formation of CHP versus time is very interesting. This is a clear indication that CHP acts as an intermediate in the reaction. As the reaction proceeds, ketone is the major products with P being formed to a much lower extent. As the formation of alcohol stops, further reaction of CHP may not yield alcohol.

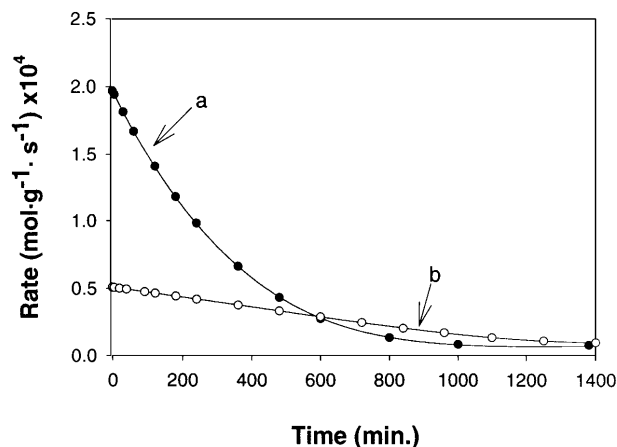


FIG. 7. Reaction rates versus time at different temperatures: a. 80°C; b. 60°C.

It seems obvious from Fig. 6 that the increase of K is at the expense of CHP after 9 h. In other words, CHP is gradually converted to K via dehydration. In a similar way, A is slowly changed to P by intermolecular dehydration of A and TBHP.

Conversion data of Figs. 3 and 5 were fit with nonlinear regression analysis to obtain an equation which was differentiated with respect to time. These differentiated data are shown in Fig. 7 which is a plot of rate versus time for reactions done at 60 and 80°C. The initial rate of reaction at 80°C is about 4 times the rate at 60°C; however, the total conversion and total yields of different products at 80°C are less than 2 times that at 60°C. These data are explained by the faster rate of decomposition of TBHP at the higher temperature. Further evidence for the decomposition of TBHP is that the efficiency of peroxide was much smaller at 80°C compared to that at 60°C during the reaction period due to faster decomposition of TBHP at higher temperature.

The reason why the initial rates (at  $t = 0$  min) are proportional to catalyst amount, whereas total conversion over the total period of reaction is not is explained as follows. The catalyst may serve as a radical initiator. Large amounts of catalyst should produce more radicals with a similar reaction mixture. A higher percentage of radicals may combine with each other to terminate the radical chain process. More radicals may also decompose peroxide than at lower radical concentration when hydrocarbon concentrations are the same. In other words, the efficiency of radicals towards oxidation may be lower at higher concentrations of radicals than at lower concentrations.

#### G. Heterogeneity of the Reaction and the Reusability of Catalysts

The liquid phase after being removed from the solid catalyst was mixed with fresh reactants and tested under similar catalytic conditions. No reaction was observed for this

TABLE 7

Effects of Solvent Amount on Cyclohexane Oxidation at 80°C for 40 h

TBA/C <sub>6</sub> H <sub>12</sub> <sup>a</sup>	% conversion	% A	% K	% CHP	% P	% selectivity of TBHP
1.40	9.18	1.72	4.28	1.66	1.52	32.5
1.60	10.4	2.20	4.53	1.66	2.02	33.1
1.80	13.1	2.83	6.57	1.38	2.36	33.5
2.00	13.0	2.92	6.84	0.94	2.31	32.9
2.20	12.7	3.07	6.14	0.93	2.52	34.1
2.50	11.6	3.45	5.54	0.56	2.10	33.8
1.80 <sup>b</sup>	12.8	3.03	6.86	0.79	2.10	

Note. A = cyclohexanol, K = cyclohexanone, CHP = cyclohexyl hydroperoxide, P = t-butyl cyclohexyl perether, catalyst: 67 mg; cyclohexane: 1.8 g; TBHP (70% aqueous solution): 2.0 g; reaction time: 40 h.

<sup>a</sup> Weight ratio of tert-butyl alcohol vs cyclohexane.

<sup>b</sup> Reaction catalyzed by used catalyst.

supernatant liquid phase. This is strong evidence that the reaction is a heterogeneous reaction.

One of the advantages of this system is the reusability of the catalysts. Similar activities were observed for the spent catalysts as shown in Table 7. The X-ray diffraction patterns of Fig. 2 show that the structure was retained after two catalytic cycles. It is clear that the structure of the catalysts is not changing. The heterogeneous reaction scheme reported here has an advantage that the catalyst can be easily separated and reused over homogeneous systems catalyzed by organometallic complexes. The heterogeneity of the reaction, the stability, and the reusability of the catalysts make this system a strong candidate for environmentally friendly practical applications.

Bressen *et al.* (37) studied the same reaction of cyclohexane oxidation by TBHP, with either phosphotungstic complexes of Ru(II) or Ru salts of tetrafluoroborate as catalysts in dimethylsulfoxide. The amount of TBHP used was a large excess as compared to substrate, and the molar ratio of TBHP to cyclohexane was as large as 10. These Ru catalysts are very active in the decomposition of TBHP. Although OMS-1 materials also exhibit some activity for TBHP decomposition, they seem to have a much lower rate than the Ru systems.

Menage *et al.* (36) reported a study of the oxidation of cyclohexane via TBHP, but with (mu-oxo) diferric complexes of bipyridine as catalysts. Since the perether was very stable and reacted only very slowly to give ketone, they believed that the perether was not a precursor to alcohol or ketone. Our system is similar to theirs (36) in this regard. However, they suggest that cyclohexanol was not a precursor to ketone which is different from our case because our yield of alcohol decreases at long reaction times (see Fig. 6).

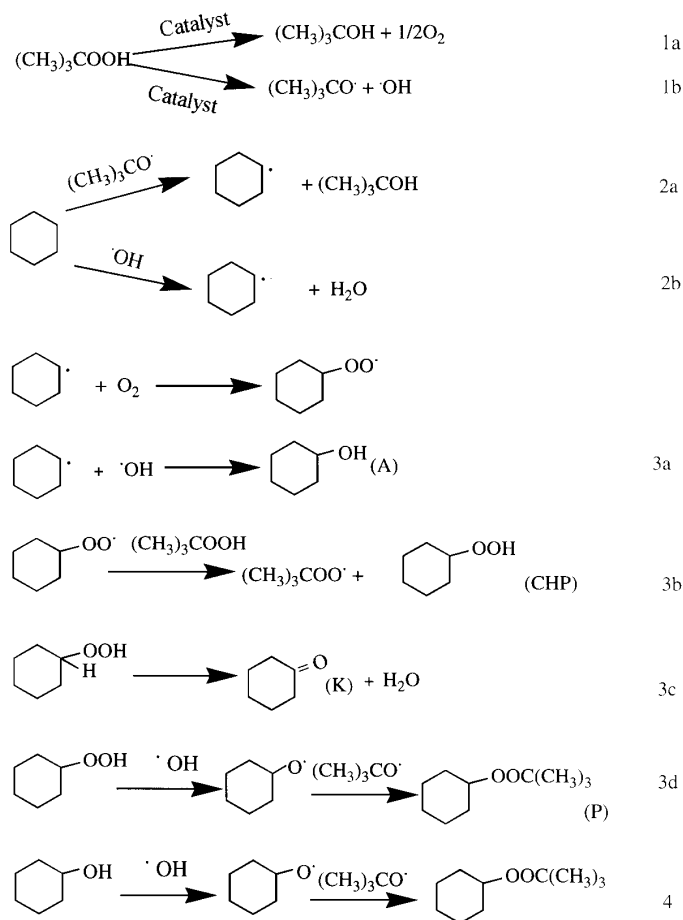
More interestingly, the (mu-oxo) diferric catalyst systems can decompose TBHP to dioxygen gas very quickly, which is a reaction that competes with the oxidation of cyclohex-

ane. Perhaps this is the reason why perether and cyclohexanol do not function as intermediates since the ratio of alcohol/ketone reached almost one when (mu-oxo) diferric complexes were used as catalysts (36).

Tateiwa *et al.* (29) also studied the oxygenation of cyclohexane via TBHP. The catalyst employed in their study is really a heterogeneous solid. They used Mn<sup>2+</sup> ion-exchanged clay as catalysts and obtained a 7.3% yield. They added an excess amount of TBHP (molar ratio of TBHP to cyclohexane of 4.5) and no t-butyl cyclohexyl perether or other products except cyclohexanol and cyclohexanone were reported. They tested commercial MnO<sub>2</sub>, and no obvious catalytic activity was found as has also been reported here.

#### H. Overall Reaction Pathways

The overall reaction pathway is believed to initially involve two parallel reactions of the peroxide reagent as shown in Scheme 1. One reaction (1a) involves the decomposition of the peroxide into alcohol (solvent) and O<sub>2</sub>. Evidence for direct decomposition of the peroxide comes from the efficiency of TBHP for oxidation of cyclohexane.



SCHEME 1



For example, based on total selectivities for the oxidation products, only 30 to 50% of the consumed TBHP is needed. These data suggest that there is a dual pathway involved where decomposition of TBHP is not useful for oxidation of cyclohexane. As more catalyst is added, there is a tendency to favor the decomposition reaction pathway. In a similar way, efficiency of TBHP decreases from around 40% to less than 31% as the reaction temperature increases from 60 to 100°C for all the doped catalysts.

The other initial pathway may involve radicals such as formation of hydroxyl and RO (reaction 1b) by the interaction of TBHP with catalyst. The reaction is believed to occur on the basis of product selectivities and the nature of peroxide.

The initial activation of cyclohexane is proposed to occur in two separate pathways as shown in reaction 2a of Scheme 1 which involves formation of a cyclohexyl radical and H<sub>2</sub>O. The other activation as shown in reaction 2b of the Scheme 1 involves formation of cyclohexyl radical and alcohol.

Product formation may be governed by the combination of radicals as shown in reaction 3a and 3b of Scheme 1. The two products (A and CHP) may serve as intermediates to form other products such as those shown in reaction 3c (K) and 3d (P). The data of Fig. 6 show a disappearance of CHP with concomitant formation of K. These data suggest that CHP is an intermediate in the formation of K. In a similar way, alcohol (A) may form radicals after loss of H from hydroxyl groups and then may combine with (CH<sub>3</sub>)<sub>3</sub>CO radical to form P (reaction 4 of Scheme 1). The data of Fig. 6 show the slow disappearance of A after 30 h of reaction and the slow increase of P over the total reaction period.

## V. CONCLUSIONS

OMS-1 materials are very active in catalyzing cyclohexane oxidation with high yields of useful functional organic compounds by using TPHP as an oxidant. Framework metal substituted OMS-1 materials are more active than OMS-1 itself. [Fe]-OMS-1 is the best framework substituted catalyst among the catalysts tested, and conversion of cyclohexane or total yield of the useful products is 13.1% (mole) at 80°C for 40 h. All the OMS-1 materials retain their crystallinity after reaction. These conversions and yields are greater than other heterogeneous catalytic cyclohexane oxidations studied under similar reaction conditions (28), and are competitive with the best homogeneous metal complex catalysts (35). However, the OMS-1 materials have reaction rates that are not as fast as the reactions catalyzed by some homogeneous metal complex catalysts. These OMS-1 heterogeneous catalysts are promising due to the high yields and ease of separation of the catalyst from the reaction product mixture.

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