

Hydrogen peroxide oxidation of aromatic hydrocarbons by immobilized iron(III)

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Abstract

Supported iron(III) ions on neutral γ -alumina are an efficient catalyst for the oxidation of aromatic hydrocarbons with hydrogen peroxide in acetonitrile at 60 °C. The catalyst is active in the low temperature liquid phase oxidation of benzene, toluene, chlorobenzene, *p*-xylene, mesitylene, benzaldehyde with hydrogen peroxide. Conversions of 31–88% with respect to starting substrate were obtained within 6 h. Oxidation on both the side chain and the aromatic ring of hydrocarbons occurred.

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1. Introduction

The selective catalytic oxidation of organic molecules continues to be a very important method for the preparation of primary and specialty chemicals in the chemical industry worldwide. Catalytic oxidation reactions using metal complexes are valuable for facilitating the development of ‘no-waste’ chemical technology based on the ‘atom economy’ principle [1,2]. The main driving force for the development of new efficient oxygenation catalysts is the necessity to functionalize feedstock alkanes to raw oxygen-containing chemicals and the ability to selectively hydroxylate non-activated C–H bonds in elaborate chemicals in order to save many steps in the preparation of fine chemicals. In addition, for obvious environmental constraints, classical stoichiometric oxidants, such as dichromate or permanganate, should be replaced by new environment friendly catalytic processes using clean oxidants like molecular oxygen or hydrogen peroxide.

In spite of the advantages of H_2O_2 as a cheap and benign oxidant, its catalytic application has some limitations due to decomposition of H_2O_2 by traces of transition metal ions [3]. Recently, we have noticed that immobilization of iron

ions on silica [4] or alumina [5], considerably retards the non-productive decomposition of H_2O_2 . Here, we report that supported iron ions on γ -alumina show remarkable catalytic properties in activation of H_2O_2 for aromatic hydrocarbons oxidation.

2. Experimental

2.1. Equipment

The reaction products were separated and identified with a Hewlett-Packard 6890 Series gas chromatograph equipped with a HP-1 capillary column (methyl siloxane 30.0 m \times 250 μ m \times 0.25 μ m) and gas chromatograph–mass spectrometry (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector). 1H NMR spectra were recorded by use of a Bruker 500 MHz spectrometer. Atomic absorptions were measured by a Varian 220 FS spectrophotometer.

2.2. Materials

The Al_2O_3 (90, active neutral, 70–230 mesh) and $FeSO_4 \cdot 7H_2O$ were purchased from Merck. Benzene and other aromatic hydrocarbons were purchased commercially and were passed through a SiO_2 column just before the

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reaction to remove oxidized impurities. Acetonitrile of the highest grade commercially available (Merck) was used without further purification. Hydrogen peroxide (35% in water) was purchased from Fluka and its concentration (11.4 M) was determined according to the standard procedure [6].

2.3. Preparation of catalyst

$\text{Fe}^{3+}\text{-Al}_2\text{O}_3$ catalyst was prepared according to the procedure described previously [5] and the iron loading was determined by measuring the amount of unloaded FeSO_4 in the solvent and the washings by atomic absorption spectroscopy (0.210 mmol FeSO_4 /1 g Al_2O_3). Normally, the catalyst was used without any pretreatment.

2.4. Oxidation of benzene; general procedure

Oxidation reactions were performed in a stirred round bottom flask fitted with a water-cooled condenser. Reactions were carried out under atmospheric pressure in air in an oil bath at $60 \pm 1^\circ\text{C}$ with acetonitrile as a solvent and aqueous H_2O_2 (35%) as an oxidant. Typically, 0.200 g of $\text{Fe}^{3+}\text{-Al}_2\text{O}_3$ catalyst (contain 0.042 mmol Fe^{3+}), benzene (1.46 mmol) and acetonitrile (4 ml) were added to the flask. After the mixture was heated to 60°C , 35% aqueous solution (1.2 ml, 13.68 mmol) of H_2O_2 was added. The typical reaction time was 6 h. After the required time, the reaction mixture was filtered and the filtrate was dried with MgSO_4 . Products were analyzed by gas chromatography, gas chromatograph–mass spectrometry, and ^1H NMR spectrometry. In order to check reproducibility each reaction was carried out twice.

3. Results and discussion

The catalyst $\text{Fe}^{3+}\text{-Al}_2\text{O}_3$ was prepared by reaction of FeSO_4 and Al_2O_3 in methanol. During this reaction, the light green color solution of Fe(II) ion in methanol changed to yellow at early moments and finally after adsorption on Al_2O_3 , a cream colored solid was obtained. Examining the filtrate by sodium thiocyanate showed the presence of Fe^{3+} ions. In a control experiment, the catalyst was prepared by using FeCl_3 instead of FeSO_4 . The resulting catalyst was similarly a cream colored solid. Examination the oxidation of benzene with H_2O_2 in the presence of these catalysts showed that they have the same activity. It turned out that the adsorbed iron ion on alumina is Fe(III) [7].

The results of preliminary experiments showed that hydrogen peroxide in the absence of catalyst does not oxidize benzene (Table 1, run 1) and that with 35% aqueous H_2O_2 , the support Al_2O_3 plays no catalytic role (Table 1, run 2). It has been reported that alumina catalyzes alkene epoxidation with anhydrous hydrogen peroxide. Alumina, however, suffers deactivation by the absorption of water [8]. Homogeneous iron(II) or iron(III) ions decompose H_2O_2 instantly at early moments of the reaction to form oxygen, so that no oxidation

Table 1

Catalytic oxidation of benzene with hydrogen peroxide^a

Run	Catalyst	Oxidant	Product yield (%)
1	None	H_2O_2	No product
2	Al_2O_3	H_2O_2	No product
3	FeSO_4^b	H_2O_2	No product
4	$\text{Fe}^{3+}\text{-Al}_2\text{O}_3$	None	No product
5	$\text{Fe}^{3+}\text{-Al}_2\text{O}_3$	H_2O_2	Phenol (27)

^a Catalyst, 0.20 g; benzene, 1.46 mmol; CH_3CN , 4 ml; H_2O_2 (35% in H_2O), 13.68 mmol; $T = 60^\circ\text{C}$; and $t = 6$ h.

^b FeSO_4 , 0.042 mmol.

product is observed (Table 1, run 3). Interestingly, the supported iron(III) ions almost do not catalyze non-productive hydrogen peroxide decomposition but activate it for oxygen transfer to aromatic compound (Table 1, run 5). These results prove that catalytic activity of $\text{Fe}^{3+}\text{-Al}_2\text{O}_3$ is due to Fe^{3+} . Large reduction in H_2O_2 decomposition by the supported iron(III) is to site isolation. The active centers for catalytic oxygen transfer attributable are formed by isolated iron species. Similarly, in oxidation of aromatic hydrocarbons with hydrogen peroxide over Zn, Cu, Al-layered double hydroxides, it has been proved that catalytically active centers are formed by isolated copper species [9]. The clustered copper ions are inactive in oxidation reaction but accelerate the decomposition of hydrogen peroxide.

In a similar manner to reported studies [10], in the presence of H_2O_2 an adduct seems to be formed which may be an $\text{Al}_2\text{O}_3\text{-Fe(III)-}\eta^1\text{-hydroperoxide}$ species stabilized by hydrogen bonding between the hydroperoxide ion and the oxygen atom of the alumina. Thus, supported iron(III) shows high activity for oxygenation of benzene with hydrogen peroxide without decomposing it.

The reaction temperature affects the catalytic performance. The conversion of benzene at 30°C is only 15%.

The effect of solvents of acetonitrile, dichloromethane, *n*-hexane, methanol, carbon tetrachloride, acetone, and ethanol on the oxidation of benzene with H_2O_2 in the presence of $\text{Fe}^{3+}\text{-Al}_2\text{O}_3$ were examined. The results of these studies are shown in Table 2. The highest conversion and

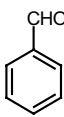
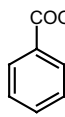
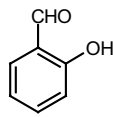
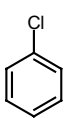
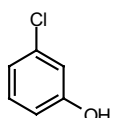
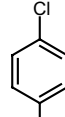

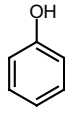
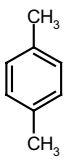
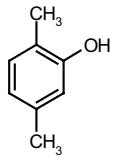
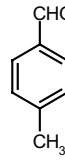
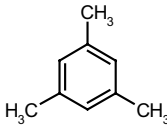
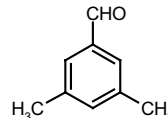
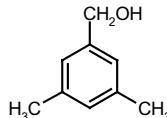
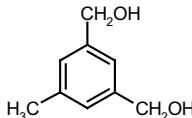
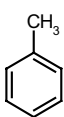
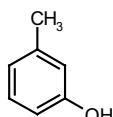
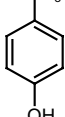
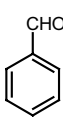
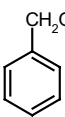
Table 2

Effects of solvents on the oxidation of benzene^a

Run	Solvent (dielectric concentration)	H_2O_2 (mmol)	Benzene conversion (%)	Phenol yield (%)
1	CH_3CN (36)	6	12	12
2	CH_2Cl_2 (8.93)	6	6	6
3	<i>n</i> - C_6H_6 (1.91)	6	1	1
4	CCl_4 (2.2)	6	2	2
5	CH_3COCH_3 (20.7)	6	33	9
6	CH_3OH (32.7)	6	27	6
7	$\text{C}_2\text{H}_5\text{OH}$ (24.3)	6	42	0

^a Catalyst $\text{Fe}^{3+}\text{-Al}_2\text{O}_3$, 0.20 g; solvent, 4 ml; benzene, 1.24 mmol; $T = 60^\circ\text{C}$; and $t = 6$ h.

Table 3
Oxidation of various aromatic compounds by $\text{Fe}^{3+}\text{-Al}_2\text{O}_3/\text{H}_2\text{O}_2/\text{CH}_3\text{CN}^a$

Number	Substrate	Conversion (%)	Product yield (%)			
1		81	 78	 2		
2		30	 16	 14		
3		27	 27			
4		24	 13	 11		
5		23	 12	 5	 3	
6		22	 8	 8	 3	 1

^a Substrate, 1.46 mmol; $\text{Fe}^{3+}\text{-Al}_2\text{O}_3$, 0.200 g (Fe^{3+} , 0.042 mmol); CH_3CN , 4 ml; H_2O_2 , 13.68 mmol (1.2 ml, 11.4 M); $T = 60 \pm 1^\circ\text{C}$; and $t = 6$ h.

selectivity was obtained in the most polar ($\epsilon = 36$) acetonitrile. Although the highest conversion of benzene was obtained in ethanol, phenol was not produced.

The conversion of benzene increased with increasing amount of hydrogen peroxide in the reaction mixture. When H_2O_2 /substrate mole ratio was about 10, the maximum conversion was obtained, showing that ca. 9 equivalents of the oxidant is decomposed in the non-productive way. This is, however, much less than the decomposition of hydrogen peroxide by unsupported transition metals [3].

To assure that the oxidation reactions catalyze by supported iron ions, a control experiment was done. The

catalytic system was filtered so that supported iron was removed from the liquid phase, and then H_2O_2 as well as benzene were further added to the obtained liquid residue. Chromatographic analysis after 6 h showed that no product was formed. Reusing the catalyst in oxidation reaction gave almost the same result as the first one.

The results of the catalytic oxidation of various aromatic hydrocarbons over the $\text{Fe}^{3+}\text{-Al}_2\text{O}_3$ carried out at 60°C are presented in Table 3. The catalytic reactions involve both the side chain oxidation and the hydroxylation of the aromatic ring. No over-oxidation of products occurred. Oxidations of phenol, anisole, nitrobenzene, naphthalene, and phenanthrene by this system were

not successful. Strong electron donating (like $-\text{OCH}_3$ or $-\text{OH}$) or electron-withdrawing (like $-\text{NO}_2$) substituents make the aromatic ring unsusceptible to oxidation by the Fe^{3+} - $\text{Al}_2\text{O}_3/\text{H}_2\text{O}_2$ system. A weakly electron-donating $-\text{CH}_3$ substituent slightly decreases aromatic ring oxidation rate. A weakly electron-withdrawing $-\text{Cl}$ substituent [11] slightly increases the conversion. Benzaldehyde has the highest conversion, 81%. The high conversion of benzaldehyde is probably due to the coordination of benzaldehyde through oxygen to supported iron to accelerate the oxidation.

The oxidation of aromatic C–H bonds via H-atom abstraction by the active oxidizing intermediate is not possible because aromatic C–H bonds are stronger than aliphatic C–H bonds [12]. In oxidation reactions, the cleavage of the oxygen–oxygen bond in peroxides takes either of two distinct pathways, heterolytic [13–15] or homolytic [16,17]. It seems that the hydroxylation of the aromatic ring occurs via the heterolytic mechanism, involving the formation of a metalloperoxide species.

4. Conclusion

The Fe^{3+} - $\text{Al}_2\text{O}_3/\text{H}_2\text{O}_2/\text{CH}_3\text{CN}$ system is a simple, cheap, and environmental friendly oxidizing system that has potential for the use in preparation of fine chemical and removal of hazardous aromatic compounds from industrial sewage.

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