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Short Communication

A synergistic effect in the combination of H_2O_2, FeAPO-5 and NaBr for selective oxidation of benzyl alcohols

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ABSTRACT

The H_2O_2/FeAPO-5/NaBr combination has been found to be active in the oxidation of benzyl alcohols. The remarkably different activity results obtained with the H_2O_2/FeAPO-5/NaBr, the H_2O_2/FeAPO-5 and the H_2O_2/NaBr confirm the existence of a strongly synergistic effect in the ternary reaction system of H_2O_2, FeAPO-5 and NaBr, leading to a significantly enhanced conversion of benzyl alcohols under mild reaction conditions.

1. Introduction

The selective oxidation of alcohols is of fundamental importance in the synthetic organic chemistry because the obtained aldehyde and ketone compounds constitute one valuable kind of precursors or intermediates used in the fine chemical, pharmaceutical and agrochemical industries [1]. Traditionally, such alcohol transformations are performed employing expensive, hazardous stoichiometric metal oxidants, *e.g.*, chromium(VI) and manganese(VII) reagents [2,3], which inevitably results in large amounts of heavy-metal waste and environmental pollutions. Catalytic alcohol oxidations with eco-friendly oxidants such as O_2 and H_2O_2 are then greatly desired and preferred for both environmental and economical benefits. So far most examples of metal-catalyzed alcohol oxidations involve the use of transition metal elements, *e.g.*, titanium [4], vanadium [5], chromium [6], manganese [7], iron [8], cobalt [9], nickel [10], copper [11], silver [12], gold [13], ruthenium [14], palladium [15], bimetallic ruthenium-copper [16] and palladium-gold [17]. Most of efforts in these studies and elsewhere have been made to immobilize or anchor these metal species as active center on an appropriate support in order to develop optimized heterogeneous catalysts for alcohol oxidations.

Aluminophosphate ($AlPO_4$) molecular sieves were originally discovered in 1982 by Wilson *et al.* [18]. Since then, the incorporation of other metal and/or non-metal elements into the framework of the pure $AlPO_4$ materials has drawn considerable attention. Research has given rise to the generation of the so-called redox molecular sieves (MeAPO-*n*) when transition metal cations (Me) are introduced into the synthesis gel and Me substitution for Al and/or P in the $AlPO_4$ framework during hydrothermal crystallization occurs [19]. For years, MeAPO-*n* molecular sieves have been found to be active, stable and selective solid catalysts for catalytic oxidations of a variety of organic substrates using O_2 and H_2O_2 as oxidants. Some excellent work includes: the aerobic oxidation of alkanes [20] and alkylaromatics [21], the H_2O_2-expoxidation of olefins [22] as well as the H_2O_2-hydroxylation of aromatics [23] and phenols [24]. As for the O_2- or H_2O_2-oxidation of alcohols catalyzed by MeAPO-*n* molecular sieves, little achievement has been made now mainly owing to low activity observed for the reaction systems although there are a few reports in this regard [22,25].

Herein, we present the informative results of the selective oxidation of benzyl alcohols as model alcoholic substrates by the H_2O_2/FeAPO-5/NaBr combination and show that as compared with the binary counterparts of the H_2O_2/FeAPO-5 and the H_2O_2/NaBr, a concerted action arising from the reaction triplet of H_2O_2, FeAPO-5 and NaBr leads to a significantly enhanced conversion of benzyl alcohols.

2. Experimental

According to the modified synthesis procedure [26], the series of FeAPO-5 molecular sieves with one-dimensional channel (pore size: 0.73 nm) was prepared by static hydrothermal crystallization of a reactive gel with molar composition $2R{:}xFe_2O_3{:}(1-x)Al_2O_3{:}1.5P_2O_5{:}240H_2O$, where R is triethylamine as an organic template agent for the AFI topology, ammonium ferric sulfate ($NH_4Fe(SO_4)_2\cdot 12H_2O$) is

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Fe source, aluminum isopropoxide Al source, phosphoric acid (85 wt.%) P source and *x* was selected as 0 (a), 0.005 (b), 0.015 (c), 0.025 (d), 0.040 (e), 0.065 (f), 0.075 (g) and 0.100 (h), respectively. The letters (a–h) here represent the synthesized samples with various Fe contents (Fig. 1). The gel was sealed in a Teflon-lined stainless steel autoclave and heated in an oven at 190 °C under autogeneous pressure for 48 h. The crystal AFI products were isolated by filtration, washed with deionized water and air dried at 120 °C for 6 h.

XRD patterns were collected at a scanning rate of 3°/min in the 2θ range of 5–50° on a D/max 2200PC Rigaku diffractometer using Cu Ka radiation ($\lambda = 0.1542$ nm) and nickel filter and operating at 40 kV and 25 mA. SEM images were obtained with a JSM-5800 scanning electron microscope. ICP-AES analysis was carried out with a Varian Vista-MPX spectrometer.

The oxidation experiments were performed under atmospheric pressure in a stirred 25-mL batch glass reactor fitted with a water-cooled reflux condenser The desired reaction temperature was achieved and maintained by a temperature-controlled water circulation system. In a typical run, 50 mg calcined FeAPO-5 catalyst was fully dispersed in 5 mL ethanol as solvent followed by an addition of 5.3 mmol benzyl alcohol (or its derivatives). After stabilization of the temperature, 0.5 mL H_2O_2 (30 wt.%, 10.6 mmol) was added in one single portion and the benzyl alcohol oxidation process was kept going with magnetic stirring for 8 h. After that, the spent solid catalyst in the reaction system was separated and removed by centrifugation. The reaction products in the clear solution obtained were analyzed by a Varian CP-3800 gas chromatograph equipped with a 25 m-long OV-17 capillary column and an FID detector.

3. Results and discussion

As shown in Fig. 1, the well-crystallized FeAPO-5 (b–h) and $AlPO_4$-5 (a) with an AFI type structure have been synthesized from the above gel composition; no XRD peaks indexed to non-AFI phase impurity were detected. A representative SEM image of as-synthesized FeAPO-5 (f) (Fe: 1.78 wt.%) further evidences high crystallinity and purity of the series of FeAPO-5 molecular sieves which is characteristic of hexagonal morphology (Fig. 2). Moreover, no changes in both the crystal structure and habit were found for the calcined FeAPO-5 molecular sieves (550 °C, 6 h); ICP-AES data show that for FeAPO-5 (b–h), the sum of the molar fractions of Fe and Al nearly approaches the molar fraction of P whereas almost the same molar fractions of Al and P were determined for $AlPO_4$-5 (a). The lattice stoichiometry of this type reveals that the isomorphous heteroatom substitution mechanism should be regarded as Fe substitution for Al in the AFI framework (for more characterization results, see supplementary material).

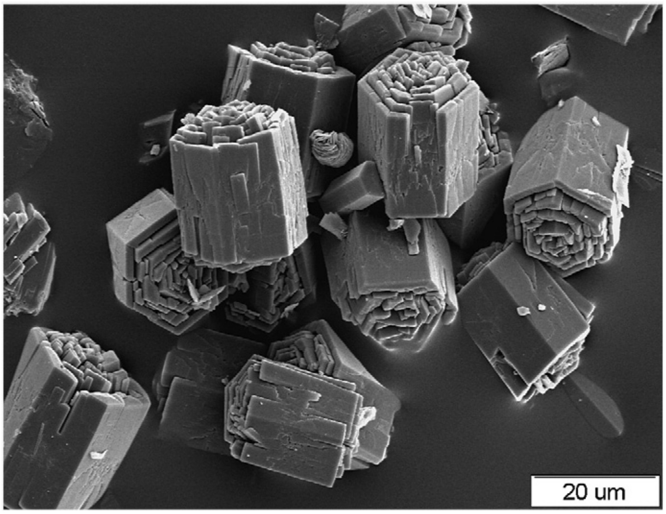


Fig. 2. SEM image of as-synthesized FeAPO-5 (f) (Fe: 1.78 wt.%).

To the best of our knowledge, this is the first report until now regarding the synthesis of FeAPO-5 molecular sieves with a wide range of Fe content and their applications in combination with H_2O_2 and NaBr, in an attempt to devise an efficient, catalytic, FeAPO-5-based reaction system for benzyl alcohol oxidations.

Comparisons of the catalytic performance of FeAPO-5 (b–h) and $AlPO_4$-5 (a) are summarized in Table 1. As shown in Table 1, only a 10% conversion of benzyl alcohol was obtained with *ca.* 85.0% selectivity to benzaldehyde for the H_2O_2/FeAPO-5 (f) and the H_2O_2/NaBr (Entries 1, 2). However, the mergence of these two binary systems into the H_2O_2/FeAPO-5/NaBr combination results in a noticeable increase in the benzyl alcohol conversion. An 82.6% conversion of benzyl alcohol with 63% selectivity to benzaldehyde was achieved with the H_2O_2/FeAPO-5 (f)/NaBr (Entry 8). Also as has been seen in Table 1, the Fe content in FeAPO-5 molecular sieves exerts an important influence on the oxidation of benzyl alcohol. As the Fe loading in

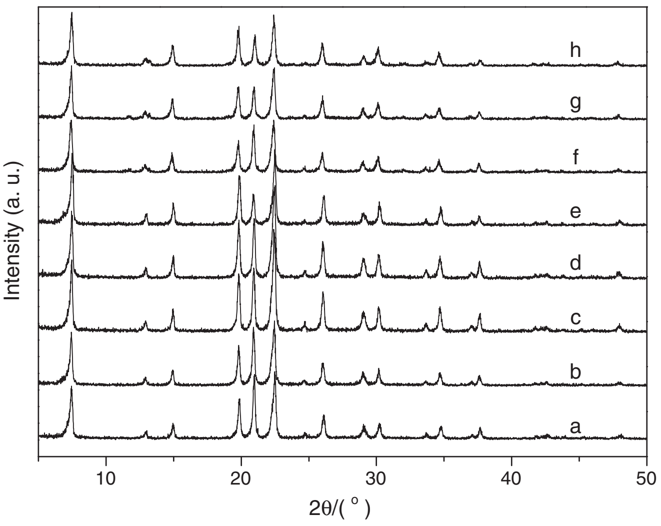


Fig. 1. XRD patterns of as-synthesized $AlPO_4$-5 (a) and FeAPO-5 (b–h): a Fe: 0.00 wt.%, b Fe: 0.21 wt.%, c Fe: 0.48 wt.%, d Fe: 0.80 wt.%, e Fe: 1.30 wt.%, f Fe: 1.78 wt.%, g Fe: 2.34 wt.%, h Fe: 2.85 wt.% (determined by ICP-AES analysis).

Table 1
Oxidation of benzyl alcohol carried out in various reaction systems [a].

Entry	Reaction system	Fe (mg) [b]	Conv. (mol%)	Sel. (mol%) [c]
1	H_2O_2/FeAPO-5 (f)	0.89	10.6	88
2	H_2O_2/NaBr	nil	11.1	83
3	H_2O_2/$AlPO_4$-5 (a)/NaBr	nil	12.4	85
4	H_2O_2/FeAPO-5 (b)/NaBr	0.11	40.2	70
5	H_2O_2/FeAPO-5 (c)/NaBr	0.24	63.9	62
6	H_2O_2/FeAPO-5 (d)/NaBr	0.40	70.6	61
7	H_2O_2/FeAPO-5 (e)/NaBr	0.65	75.1	62
8	H_2O_2/FeAPO-5 (f)/NaBr	0.89	82.6	63
9	H_2O_2/FeAPO-5 (g)/NaBr	1.17	74.7	56
10	H_2O_2/FeAPO-5 (h)/NaBr	1.43	70.0	52
11	H_2O_2/Fe(III)/NaBr [d]	0.89	15.8	61

[a] Reaction conditions: reaction temperature (70 °C), reaction time (8 h), FeAPO-5 catalyst (50.0 mg, calcined at 550 °C for 6 h), benzyl alcohol (5.3 mmol), benzyl alcohol/H_2O_2 molar ratio (1 : 2), solvent (ethanol, 5 mL), [NaBr] (0.1 M). H_2O_2 was added in one single portion and no oxidation of ethanol was observed in the blank experiment.

[b] The Fe loading values in the reaction systems were calculated by multiplying the amount of catalyst (50.0 mg) by the corresponding Fe content (wt.%) of catalyst.

[c] The remaining product was benzoic acid.

[d] The same amounts of H_2O_2, Fe(III) and NaBr and the same reaction conditions (as those chosen for the H_2O_2/FeAPO-5 (f)/NaBr combination) were adopted in the homogeneous reaction system of H_2O_2, Fe(III) and NaBr.

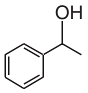
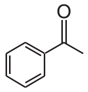
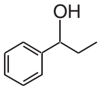
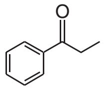
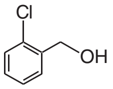
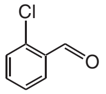
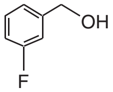
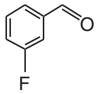
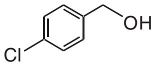
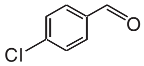
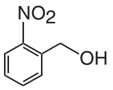
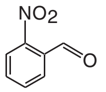
the reaction systems was varied over the range of nil to 0.89 mg, a sharp increase in the conversion of benzyl alcohol took place, yielding a variation of benzyl alcohol conversion from 12.4% to 82.6% (Entries 3–8). Compared with the H_2O_2/$AlPO_4$-5 (a)/NaBr (Fe loading: nil), the superior catalytic behavior exhibited by the H_2O_2/FeAPO-5/NaBr can be reasonably attributed to the presence of the redox metal iron in the AFI framework of FeAPO-5 molecular sieves. Furthermore, the H_2O_2/FeAPO-5 (g)/NaBr and the H_2O_2/FeAPO-5 (h)/NaBr with higher Fe loadings gave relatively lower conversions of benzyl alcohol with lower selectivity to benzaldehyde (in comparison with the H_2O_2/FeAPO-5 (f)/NaBr, Entries 8–10) because of the increased formation of benzoic acid and the more severe decomposition of H_2O_2 under the chosen reaction conditions.

The Fe leaching experiment was performed to ascertain if the reaction is truly heterogeneous: the conversion of benzyl alcohol (35.3%) remained unchanged after filtering off the FeAPO-5 (f) catalyst (70 °C, 2 h) and letting the reaction continue for the rest of reaction period (6 h); ICP-AES analysis also shows no observable changes of Fe contents in both fresh and spent catalysts. These phenomena indicate that the oxidation of benzyl alcohol indeed goes through a heterogeneous catalytic reaction process. In addition, any iron which leached into the liquid phase in the reaction system is not concluded to be homogeneously active due to the fact that only a 15.8% conversion of benzyl alcohol was obtained in the homogenous reaction system composed of H_2O_2, Fe(III) and NaBr (Entry 11) containing the same amounts of the above three reaction reagents as those used in the H_2O_2/FeAPO-5 (f)/NaBr combination.

Moreover, some additional observations were made as follows: (1) the presence of bromine (Br_2) in the reaction system was demonstrated by a light brown coloration which developed during the oxidation of benzyl alcohol with the H_2O_2/FeAPO-5/NaBr; (2) addition of equivalent amount of cyclohexene (5.32 mmol) as the competing substrate into the reaction system deeply suppressed the oxidation of benzyl alcohol and the formation of 1, 2-dibromocyclohexane was detected by GC–MS analysis, implying that Br_2 is a key intermediate species involved in the oxidation of benzyl alcohol; (3) no appreciable, irreversible consumption of NaBr was found during the oxidation of benzyl alcohol because post-reaction addition of aqueous $AgNO_3$ solution into the liquid phase reaction mixture free of the spent FeAPO-5 catalyst prompted a quantitative precipitation of AgBr.

In summary, the concomitant presence of H_2O_2, FeAPO-5 and NaBr seems clearly to be a prerequisite for the high efficiency of in the oxidation of benzyl alcohol. As is well known, H_2O_2 has a higher redox potential ($E^{\theta}_{a,\ H_2O_2/H_2O} = 1.77$ V) than HOBr ($E^{\theta}_{a,\ HBrO/Br^-} = 1.33$ V) and the latter reagent very easily reacts with Br^- to afford Br_2; Br_2 added directly or generated *in situ* is capable of oxidizing alcohols into their corresponding carbonyl compounds; such alcohol oxidations have been confirmed to proceed through a mechanism in which the rate-determining step involves a hydride transfer by Br_2 from the OH-bearing carbon followed by a rapid proton removal from the oxygen [27–29]. Also based on the observations here, the reaction steps involved in this oxidative transformation can be diagrammed in Scheme 1.

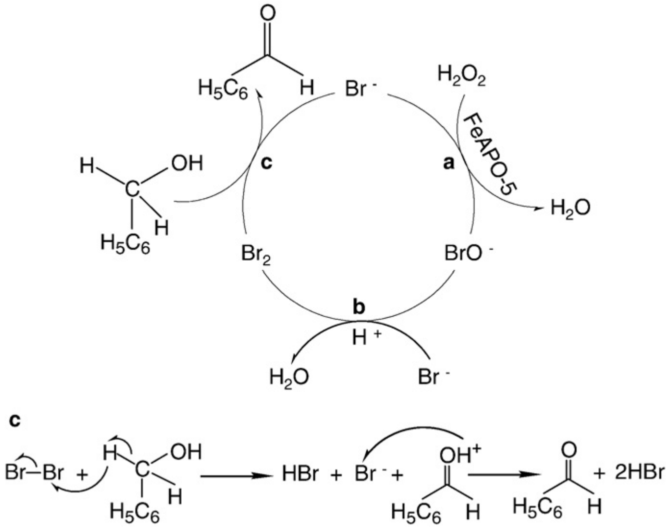
Table 2
Oxidations of other benzyl alcohols with the H_2O_2/FeAPO-5(f)/NaBr [a].

Substrate	Product	Conv. (mol%) [b]	Sel. (mol%)
		56.2	100
		60.1	100
		83.2	57[c]
		52.1	54[c]
		61.3	58[c]
		40.8	88[c]

[a] The same reaction conditions as those of Table 1 were adopted in Table 2.

[b] Around 5–10% conversions of benzyl alcohols were obtained with the binary reaction systems of the H_2O_2/FeAPO-5 (f) and the H_2O_2/NaBr.

[c] The remaining products were the corresponding benzoic acids.



Scheme 1. Reaction steps involved in the oxidation of benzyl alcohol with the H_2O_2/FeAPO-5/NaBr combination.

Therefore, the nature of the H_2O_2/FeAPO-5/NaBr for the oxidation of benzyl alcohol can be described as subsequently: FeAPO-5 molecular sieves first catalyze the H_2O_2—oxidation of bromide ion to HBrO/BrO^-; the newly formed HBrO/BrO^- then reacts with bromide ion to yield bromine; as for the last step in the overall reaction scheme, the formation of benzaldehyde involves the bromine-mediated hydride ion abstraction as mentioned earlier, with being accompanied by regeneration of bromide ion and initiation of another reaction cycle.

The scope of the H_2O_2/FeAPO-5/NaBr can be partly illustrated by Table 2 in which oxidations of several other benzyl alcohols were also investigated under the same reaction conditions. As with benzyl alcohol, the selected benzyl alcohols can readily undergo oxidation into the corresponding aldehydes or ketones with moderate to high conversions.

4. Conclusions

To summarize, we have found an interesting reaction feature of the H_2O_2/FeAPO-5/NaBr combination which derives itself from the synergistic effect among H_2O_2, FeAPO-5 and NaBr, and can be utilized for the oxidation of benzyl alcohols. Although the limited reactivity needs further improving, we wish that our present work can provide an alternative design methodology for the development of new, efficient, catalytic reaction systems for syntheses of carbonyl compounds and other useful organic products.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.09.035.

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