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COMMUNICATION

Iron-Catalyzed Oxidative Functionalization of C(sp^3)–H Bonds under Bromide-synergized Mild Conditions†

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The efficient oxidation and functionalization of C-H bonds with an inorganic-ligand supported iron catalyst and hydrogen peroxide to prepare the corresponding ketones was achieved using bromide ion as a promoter. Preliminary mechanistic investigations indicated that the bromide ion can bind to the $FeMo_6$ form a supramolecular species ($FeMo_6$·2Br), which can effectively catalyze the reaction.

The selective catalytic C(sp^3)-H oxidation using transition-metal complexes and environmentally benign oxidants (e.g., H_2O_2) under mild conditions are greatly desired because carbonyl group are highly useful building blocks for a number of subsequent transformations in organic synthesis[1]. In this context, several transition metals such as iron[2], palladium[3], copper[4], cobalt[5], manganese[6], and iridium[7], have been intensively investigated for C-H oxidation processes. However, a common feature in these catalytic systems is the use of complex and inconvenient organic ligands to improve the catalytic activity and selectivity. Although a few iron salts[8] and biocatalytic[9] approaches achieved have been disclosed but suffer from scope limitations. Moreover, the durability and recyclability of organometallic catalysts under mild conditions remains a major challenge in industrial and synthetic chemistry due to the susceptibility of the organic ligands to undergo oxidative self-degradation. Therefore, the innovation and improvement of catalytic methods with other ligand supported iron catalysts,[10a,b] which provides an alternative approach to the use of structurally complex ligand systems, is highly desired.

Polyoxometalates (POMs)[10, 11], as a class of metal-oxide clusters with unmatched structural diversity and functionality, are considered to be an inorganic alternative to classical transition-metal complexes. The catalytic function of POMs has attracted much attention because their ability to design catalytically active sites allows for 'fine-tuning' of their redox and acidic properties at the atomic or molecular levels[12]. Recently, our group reported that Anderson-type POMs[13] can be used as the inorganic ligand-supported metal catalysts for the highly efficient aerobic oxidation of aldehydes to formamides[14a], amines to imines[14b], carboxylic acids[14c], or alcohols to aldehydes[14d]. These types of inorganic ligand-supported metal catalysts possess a unique structure with a single central metal atom supported by an inorganic ring made up of six edge-sharing $Mo^{VI}O_6$ octahedral scaffolds; this greatly enhances the Lewis acidity of catalytically active sites, as well as enables the edge-sharing MoO_6 unit to act as ligands analogous to those used in traditional organometallic complexes. Inspired by this, the versatile tunability of Anderson-type POMs prompts us to further extend the scope of this type of catalysts for other catalytic oxidation transformations.

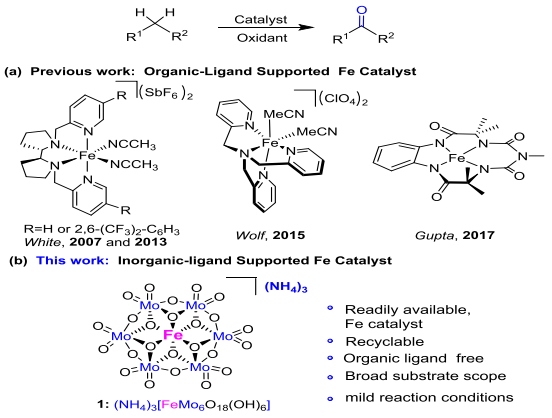

Fig.1 Fe Catalyst for C(sp^3)-H oxidation

Herein, we report that using 30% H_2O_2 as the sole oxidant, an inorganic-ligand supported iron catalyst **1**, $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ (Fig. 1b), which possess an iron(III) ion core and can be readily synthesized in one pot in aqueous solution at 100°C (see SI, Fig. S1-S3), can efficiently catalyse the oxidation of various methylene C–H bonds with high catalytic activity and selectivity. More importantly, **1** could be recycled and reused for at least six times with negligible loss of activity due to high stability. One of the main advantages of this catalytic system is that it can avoid the use of complicated/sensitive organic ligands.

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Mechanistic insight based on the observation of key intermediate and control reactions will be also presented.

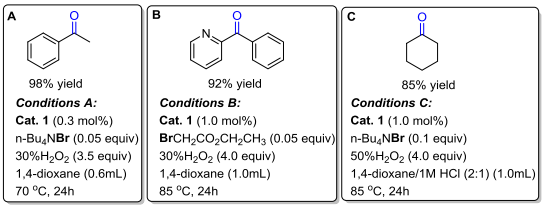

Fig.2 Evaluated iron catalyst with three types of substrates[a].

We initially evaluated the iron catalyst using three typical compounds containing methylene C-H bonds as the model substrates toward the oxidation reaction, including activated aromatic ethylbenzene, low activated *N*-heterocyclic 2-benzylpyridine and inert aliphatic hexane. The reaction of activated ethylbenzene (1.0 mmol) with 30% H_2O_2 as the oxidant and *n*-Bu_4NBr (0.05 equiv) as an additive in the presence of **1** (0.3 mol%) at 70 °C resulted in the formation of acetophenone in 96 % yield after 24 hours. (Conditions A, for more details, see Fig. 2 and Table S3). Unfortunately, this method was ineffective for the oxidation of 2-benzylpyridine owing to the more electronegative nitrogen in the pyridine ring, making the adjacent CH_2 more inactive, which leads to poor selectivity[15]. To solve these problems, we decided to introduce ethyl bromoacetate to react with 2-benzylpyridine, which can generate a covalent C-N bond to increase the acidity of hydrogen atoms in the methylene group. This process would activate the C-H bond in the methylene group and the activating group is reduced and removed from the N-heterocyclic compound when the N-heterocyclic ketone is formed. To our delight, 2-benzylpyridine was selectively oxidized to afford 90% yield of the desired product (Conditions B, for more details, see Fig. 2 and Table S4). When the reaction mixture was investigated by GC-Ms, ethyl bromoacetate was found to be converted to ethyl acetate. A small number of α-halogen compounds were subjected to the oxidation of the aliphatic C-H bond, and a positive results were obtained (SI, Table S4, entries 4–7). For the inert cyclohexane, our strategy is to increase the concentration of hydrogen peroxide to enhance the activity of the catalytic system, and 85% cyclohexanone was obtained (Conditions C, for more details, see Fig. 2 and Table S5). It was important to realize that bromine element is essential for the selective oxidation of the C-H bond of three types of substrates.

To explore the key role of the bromide ion in the reaction system, the reaction was examined by single crystal X-ray diffraction and electrochemistry techniques (SI, Fig. S5, Table S1 and Table S2). Single-crystal X-ray diffraction analysis suggested that the bromide ion can bind to the iron catalyst *via* multiple hydrogen bonds to form a supramolecular species ($FeMo_6$·2Br) structure in the crystalline state. The bromide ion binding effect on the redox properties of the iron catalyst has been evaluated using electrochemistry techniques. Upon addition of *n*-Bu_4NBr or ethyl bromoacetate, the redox peak shifts towards a more positive potential, indicating that Br^- greatly improves the electron transfer efficiency due to the strong electronic interaction between the iron catalyst and bromide ion. Thus, it can be seen from the CV studies that the hydrogen bonds between $FeMo_6$ and bromide ion significantly alter the electrochemical properties of the catalyst system (see SI, Fig. S6).

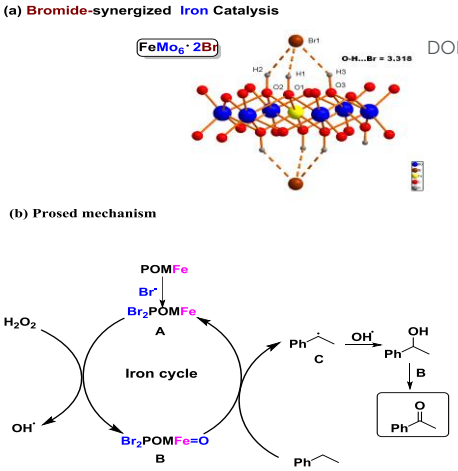

Fig.3 Mechanism study of the catalytic C(sp^3)-H selective oxidation. (a) Bromide-synergized Iron Catalysis (b) Plausible reaction mechanism.

To gain insight into the mechanism, a series of control experiments were conducted. The addition of typical radical scavengers such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or butylated hydroxytoluene [2,6-di-tert-butyl-4-methylphenol (BHT)] inhibited the reaction, suggesting that a mechanism involving the radical is operative (Fig. S4(1)). When $FeMo_6$·2Br was employed stoichiometrically under an inert atmosphere, this complex did not form any oxidation product upon reaction with ethyl benzene, indicating that $FeMo_6$·2Br is not an activated oxidant (Fig. S4(2)). When the reaction was stopped after 12 hours, the oxidation product acetophenone and radical adducts 1-phenethyl alcohol were both observed in 64% and 36% yields, respectively (Fig. S4(3)). When phenethyl alcohol was subjected to the standard reaction conditions **A**, the corresponding product acetophenone was also obtained in 97% yield (Fig. S4(4)). These results indicated that this transformation might involve 1-phenethyl alcohol as the reaction intermediates.

Based on the above results and previous reports[2, 16], a possible reaction pathway is proposed (Fig. 3b). Initially, the iron catalyst reacts with bromide ion *via* multiple hydrogen bonds to form **A.** In the presence of H_2O_2, **A** is oxidized to complex **B** and afford the hydroxyl radical. Ethyl benzene is directly oxidized by **B** to afford the radical species **C**. Subsequently, radical species **C** easily combines with hydroxyl radical to form the benzylic alcohols. Finally, the benzylic alcohols subsequently undergoes a second oxidation by complex **B** to give the acetophenone.

With the optimized conditions in hand, various substituted ethyl arenes were subjected to the Iron-catalyzed oxidation of aliphatic C-H bond to test the substrate cope and generality (Table 1). Ethylbenzene derivatives with different substituents on the aromatic rings have been selectively oxidized to the corresponding ketones with good-to-excellent yields (compounds **2-10**).

The reaction of H_2O_2 with ethylbenzene derivatives bearing electron-rich groups afforded the corresponding ketones in good yields (compounds **3-5**), while ethylbenzene bearing electron-deficient groups gave slightly diminished yields (compounds **6-10**). The reactions proceeded with good yields in the presence of 4-ethyl-1,1'-biphenyl and 1-

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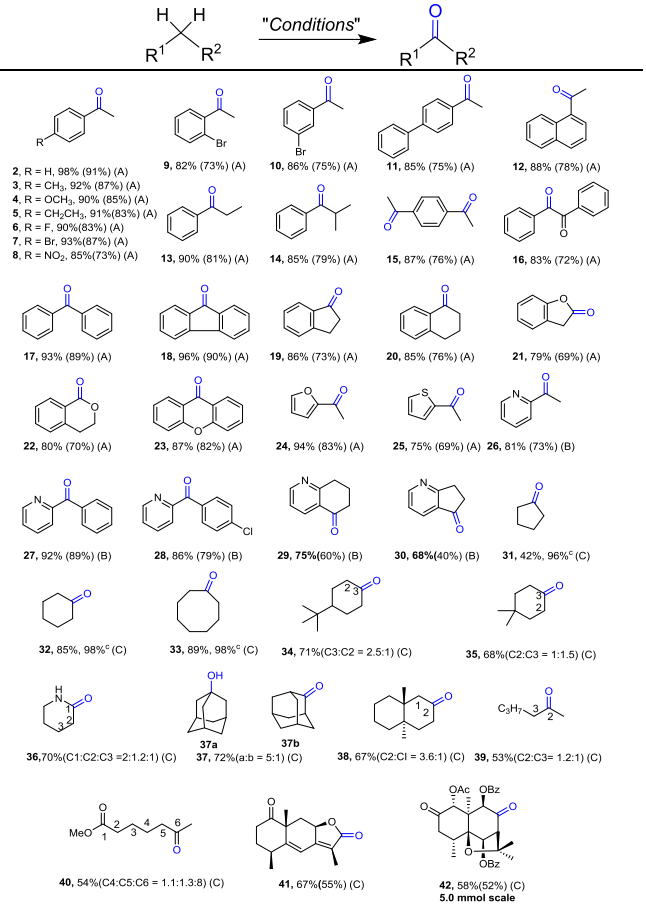
ethylnaphthalene (compounds **11** and **12**). This method was also successfully applied to long-chain aliphatic benzylic positions derivatives, providing the corresponding products in 90% and 85% yields (compounds **13** and **14**). Others benzylic positions such as 1,4-diethylbenzene, 1,2-diphenylethan-1-one and diphenylmethane was well tolerated (compounds **15-17**).

Table 1. Selective oxidation of C-H bonds to ketones catalyzed by 1[a,b]



[a]Reaction condition A (compounds **2-25**): aromatic ethylbenzene (1.0 mmol), Cat. **1** (0.3 mol%), 30% H_2O_2 (3.5 equiv.), TBAB (0.05 equiv.), 1,4-dioxane (0.6 mL) at 70 °C for 24 h. reaction condition B (compounds **26-30**): *N*-heterocyclic 2-benzylpyridine (1.0 mmol), Cat. **1** (1.0 mol%), 30% H_2O_2 (4.0 equiv.), $BrCH_2CO_2CH_2CH_3$ (0.05 equiv.), 1,4-dioxane (1.0 mL) at 85 °C for 24 h. reaction condition C (compounds **31-42**): aliphatic hexane(1.0 mmol), Cat. **1** (1.0 mol%), 50% H_2O_2 (4.0 equiv.), TBAB (0.1 equiv.), 1,4-dioxane/1M HCl (2:1)(1.0 mL) at 85 °C for 24 h. [b,c] Yields and selectivity were determined by GC-Ms analysis of the crude reaction mixture, values in parentheses are the isolated yields. compounds **41** and **42,** Yields were determined by ^{1}H-NMR, values in parentheses are the isolated yields.

The reaction of aromatic hydrocarbons bearing a methylene moiety in cyclic framework proceeded smoothly to afford the desired products in 85–96% yield (compounds **18-20**). Also, alkoxy C-H bonds were oxidized effectively (compounds **21-23**). Heteroaromatic benzylic positions containing oxygen or sulfur, which are well known to poison organometallic catalysts due to their strong coordination to the metal center, could also be transformed into the corresponding ketones in good yields (compounds **24** and **25**).

After the successful application of the oxidative reaction of benzylic methylene, we tried to extend this process to build up structurally important pyridine. The reaction with 2-ethylpyridine proceeded to afford the desired products in 81% yield (compound **26**). Furthermore, 2-benzylpyridine and 2-(4-chlorobenzyl)pyridine were also suitable for this reaction (compounds **27** and **28**). In addition, 5,6,7,8-tetrahydroquinoline and 6,7-dihydro-5H-cyclopenta[b]pyridine reacted with 30% H_2O_2 under the standard conditions to afford the desired products in moderate yields (compounds **29** and **30**).

The problems faced are well highlighted in the selective oxidation of alkyl aliphatic, a longstanding challenge in oxidation catalysis. The strength of their C-H bonds (~96 kcal mol^{-1}) coupled with the lack of appreciable differences in electronic and steric properties makes the internal methylenes practically indistinguishable. Encouraged by the high reactivity of aromatic and *N*-heterocyclic methylene C-H bonds oxidation reaction using our methodology, a series of inert aliphatic were tested. The reaction with smaller cycloalkanes could be oxidized in low yields (compound **31**, 42%), but larger cycloalkanes were converted into the corresponding ketones in good yield(compound **32**, 85% and **33**, 89%). In substituted cyclohexanes, both distal positions 2° and 3° were successfully oxidized, with a preference for the 3° position (compounds **34** and **35**). To our surprise, piperidine could also be utilized to prepare desired products in 70% yield (C1:C2:C3 =2:1.2:1) (compound **36**). Adamantane could be oxidized, yielding the tertiary C–H bonds product (compound **37a**), along with the secondary product (compound **37b**; 72% yield, 5:1 selectivity). With trans-decalin, both the positions 2° and 3° were oxidized in a 3.6:1 ratio (compound **38**, 67%). With *n*-Hexane, it was oxidized with no site selectivity (primary C–H bond oxidation has not been observed with **1**), forming positions 2° and 3° ketones in a 1.2:1 ratio (compound **39**). The carboxylate group on the substrate such as methyl heptanoate was oxidized into ketones in a normalized 1.1:1.3:8 C4:C5:C6 mixture with 54 % combined yields (compound **40**). The capacity of this method to selectively modify natural scaffolds was demonstrated by the selective oxidation of 1β-hydroxy alantolactone in synthetically useful yields (compound **41**). Our method enabled the selective oxidation of allylic positions, thus highlighting the mild nature of this oxidation method and highly predictably selective of iron catalyst. Finally, the utility of our oxidation protocol was convincingly demonstrated by the scalable oxidation of dihydro-β-agarofuran in good yield (compound **42,** 58%, 5 mmol scale).

The stability and recyclability studies for the iron catalyst have been established by recycling experiments. Ethylbenzene was oxidized using Mo_6Fe and hydrogen peroxide as the sole oxidant. After the completion of the reaction, the Mo_6Fe catalyst was recovered, washed with ether and reused for the fresh oxidation of ethylbenzene. This process could be repeated at least six times with little loss of the activity (see SI, Fig. S7). As confirmed by FTIR and XRD, the recycled catalyst remains almost unchanged from its original state (see SI, Fig. S8 and Fig. S9).

Conclusions

In conclusion, it has demonstrated that bromide ion can promote the selective oxidation and functionalization of the methylene C(sp^3)-H

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bonds to prepare the corresponding ketones with an inorganic-ligand supported iron catalyst and hydrogen peroxide. Synergistic interaction between the bromide ion and iron complex via multiple hydrogen bonds to form a supramolecular compound ($FeMo_6{\cdot}2Br$) could activate the C-H bonds of the methylene group to easily prepare the ketones. The study of the substrate scope shows that both activated and un-activated aliphatic C-H bonds (41 examples) compounds, including natural scaffolds such as 1β-hydroxy alantolactone and dihydro-β-agarofuran, have been converted into the corresponding ketones with high selectivity and good to excellent yields by using hydrogen peroxide as the oxidant. Furthermore, the iron catalyst is stable and recyclable, and can be easily prepared by a simple one-step synthesis from simple inorganic metal salts. Importantly, the effect of bromide ion could provide valuable information for the further design of additives for selective iron-catalyzed direct oxidation and functionalization reactions of C(sp^3)-H bonds.

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Conflicts of interest

In There are no conflicts to declare.

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