NJC

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
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Cite this: *New J. Chem.*, 2021, **45**, 3683

Metal nitrate-catalyzed one-pot oxidative esterification of benzaldehyde with hydrogen peroxide in alcoholic solutions at room temperature

Márcio José da Silva * and Cesar Macedo de Oliveira

Received 20th November 2020,
Accepted 20th January 2021

DOI: 10.1039/d0nj05671e

rsc.li/njc

The activity of metal nitrate catalysts was investigated in the oxidative esterification reactions of benzaldehyde with hydrogen peroxide. Several types of metal nitrates (alkaline, alkaline earth, and transition metals) were evaluated as catalysts. Among the assessed salts, $Fe(NO_3)_3$ was the most efficient catalyst toward the formation of the target product (*i.e.*, benzoic alkyl ester). In methyl alcohol, benzaldehyde was selectively oxidized to benzoic acid and then esterified to methyl benzoate. The efficiency of the catalyst was correlated with its higher Lewis acidity character, which was established through the pH measurements of methanolic solutions of the soluble metal nitrate salts. The influence of main variables of the reaction, such as catalyst load, temperature, and reactant stoichiometry, was investigated. The size of the carbon chain and steric hindrance played an essential role in the reaction selectivity. While methyl and ethyl alcohols selectively provided ester as the main product (*ca.* 70–75%) and acetal as the subproduct, the other alcohols gave ester, hemiacetal, and benzoic acid, which was formed in the least amount. The use of an inexpensive catalyst, a green oxidant, mild conditions, and short reaction times were the positive aspects of this one-pot process. The high TON (*ca.* 900) is evidence of the high catalytic activity of $Fe(NO_3)_3$. It is noteworthy that this methodology does not rely upon ligands and other additives.

Introduction

The production of benzoic esters has raised a lot of interest, due to the extensive use of these products as a raw material in the industrial production of polymers, cosmetics, perfumes, fibers, plasticizers, and dyes.[1,2] In particular, the one-pot conversion of aromatic aldehydes to esters has been demonstrated to be an attractive route to synthesize esters.[3]

Stoichiometric oxidation processes commonly employs toxic reactants such as *N*-bromosuccinimide/pyridine, diazonium salts, or chromium trioxide.[4] Alternatively, Lewis acid metal have been used as catalysts in oxidation reactions with environmentally benign oxidants like hydrogen peroxide.[5] In this sense, hydrogen peroxide has received considerable attention because it is an atom-efficient, non-flammable, and easy to handle oxidant, which generates only water as the by-product.[6,7]

Various oxidative processes of organic compounds with aqueous hydrogen peroxide have been developed in the presence of an adequate solvent, avoiding the use of a phase transfer agent, as well as the addition of pH controllers.[8–11] Notwithstanding, hydrogen peroxide requires an activation step, which is performed by metal catalysts. Various organometallic compounds have been successfully used as catalysts in the oxidative esterification of aldehydes.[12–17] Nonetheless, their high cost, the difficult synthesis, and their thermal instability are negative aspects of their use.

It is known that solid supported catalysts activate hydrogen peroxide in solution, and are an attractive option to oxidize alcohols and aldehydes.[18–22] For instance, Thakur *et al.* assessed the activity of titania-supported $VO(acac)_2$ in the oxidation of aromatic and aliphatic aldehydes with hydrogen peroxide to methyl esters.[23] Although the immobilization of homogeneous catalysts on a solid support is a widely explored field, there are some drawbacks that motivate the search for a better understanding of how these catalysts act in solution.[24] Notwithstanding, the study of catalytic activity of the transition metal salts in solution has been useful to optimize their use as heterogeneous catalysts.[25,26] In this sense, polyoxometalates such as transition metal salts of heteropolyacids of Keggin type have been widely used as catalysts in oxidation reactions with hydrogen peroxide.[27–30]

In addition to transition metals, calcium and magnesium chlorides were also found to be efficient catalysts in the oxidative

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Chemistry Department, Federal University of Viçosa, Viçosa, Minas Gerais State, 36590-000, Brazil. E-mail: silvamj2003@ufv.br; Fax: +55-31-3899-3065; Tel: +55-31-3899-3210

esterification of benzaldehydes; however, the reactions were slow (*ca.* 24–48 h).[31] Among the series of metal salts assessed in oxidative esterification of benzaldehyde in the CH_3OH/H_2O_2 system at room temperature, zinc bromide was the most active and selective toward methyl esters; however, the reactions required a long time (*ca.* 16 h), besides a high catalyst load (*ca.* 10 mol%), to achieve good yield.[32] Iron salts (*i.e.*, halides, acetate, acetylacetonate, perchlorate, sulfate anions) were also investigated in similar reactions, but with ethyl alcohol, and $Fe(ClO_4)_3$ was found to be the most active catalyst; however, a reaction time of 20 h and a high catalyst load (10 mol%) were again required.[33]

In the present study, for the first time as far as we know, metal nitrate salts are used as catalysts in oxidative esterification reactions of benzaldehyde with hydrogen peroxide in alcoholic solutions. The focus was on correlating the activity and selectivity attained in metal nitrate-catalyzed reactions with the main reaction parameters (*i.e.*, oxidant load, type and concentration of metal nitrate catalyst, temperature, and nature of alcohol). Simple experimental data such as pH measurements and product selectivity allowed us to propose reaction pathways that elucidated how the most active catalyst (*i.e.*, $Fe(NO_3)_3$) contributed to converting benzaldehyde into alkyl ester.

Experimental

Materials and methods

All chemicals were commercially available and were utilized without prior treatment. $LiNO_3$ (99 wt%), $Co(NO_3)_2{\cdot}6H_2O$ (98 wt%), $Mn(NO_3)_2{\cdot}4H_2O$ (98 wt%), $Cu(NO_3)_2{\cdot}3H_2O$ (98 wt%), $Ni(NO_3)_2{\cdot}6H_2O$ (98 wt%), $Ba(NO_3)_2$ (99 wt%), and $Mg(NO_3)_2{\cdot}2H_2O$ (99 wt%) were obtained from Dinamica Ltd (Brazil). $Fe(NO_3)_3{\cdot}9H_2O$ (98 wt%), $FeCl_3{\cdot}6H_2O$ (98 wt%), $FeSO_4{\cdot}7H_2O$ (98 wt%), $Fe_2(SO_4)_3{\cdot}5H_2O$ (98 wt%), $Zn(NO_3)_2{\cdot}6H_2O$ (98 wt%), $Sr(NO_3)_2$ (99 wt%), $Al(NO_3)_3{\cdot}6H_2O$ (99 wt%), and $AgNO_3$ (99 wt%) were acquired from Vetec (Brazil). Benzaldehyde (*ca.* 99 wt%) and alkyl alcohols (*i.e.*, methyl, ethyl, propyl, isopropyl, butyl, *sec*-butyl and isobutyl; *ca.* 99.0–99.5 wt%) were obtained from Sigma-Aldrich. Hydrogen peroxide was purchased from Vetec (*ca.* 34 wt% aqueous solution).

Catalytic tests

Catalytic runs were performed under magnetic stirring in a glass reactor (*ca.* 50 mL), fitted with a reflux condenser and sampling septum, in a glycerine bath. Typically, benzaldehyde (*ca.* 10 mmol) and metal nitrate catalyst (*ca.* 10 mol%) were dissolved in CH_3OH (*ca.* 10 mL solution), at room temperature (*ca.* 298 K). After the slow addition of aqueous H_2O_2 solution (*ca.* 30 mmol), the reaction was started.

The reaction progress was monitored by GC analysis of samples periodically collected (GC 2010 Shimadzu, capillary column, FID). The reaction products were identified by GC-MS analysis (GC-MS 2010 ultra mass, *i.e.* 70 eV), and comparison with chromatographic analytical standards. The main response factors in relation to benzaldehyde were as follows: benzoic acid (1.1), methyl benzoate (1.0), ethyl benzoate (1.0), propyl benzoate (0.9), and butyl benzoate (0.8).

The acidity of the medium was used to verify the relation between the Lewis acidity of the catalyst salt and the decrease triggered by its addition to the reaction solution. For this, the pH was measured before and after the addition of hydrogen peroxide to the reaction solutions, using a potentiometer (Bel pH meter, model W3B) with a glass electrode. Before each measurement, the pH meter was calibrated at pH 4.0 and 6.86, using potassium hydrogen phthalate and dihydrogen/hydrogen phosphate NIST buffers, respectively.

Typically, the catalyst salt (*ca.* 10 mol% relative to benzaldehyde) was added to alcohol methyl solution, and magnetically stirred until pH stabilization was reached. The effect of peroxide addition on the pH of reaction solutions was also verified in the presence of each catalyst salt.

Results and discussion

Screening of the metal nitrate catalyst

In this work, our initial objective was to select the most active and selective catalyst in the oxidative esterification of benzaldehyde with hydrogen peroxide in metal nitrate-catalyzed reactions carried out in methyl alcohol solution. The catalyst load (*ca.* 10 mol%) was selected based on the literature.[31–33]

It is important to highlight that the reaction conditions were not optimized to achieve the maximum conversion, as our aim was to select the most active catalyst (Fig. 1).

In general, when the catalyst was active, benzaldehyde was oxidized to benzoic acid and quickly esterified to methyl benzoate; these two reactions occurred in a one-pot process, in the presence of aqueous H_2O_2, and in methyl alcohol solutions containing catalytic amounts of the metal nitrate. However, depending on the cation present in the nitrate salt, a concurrent reaction occurred (*i.e.*, condensation of benzaldehyde with

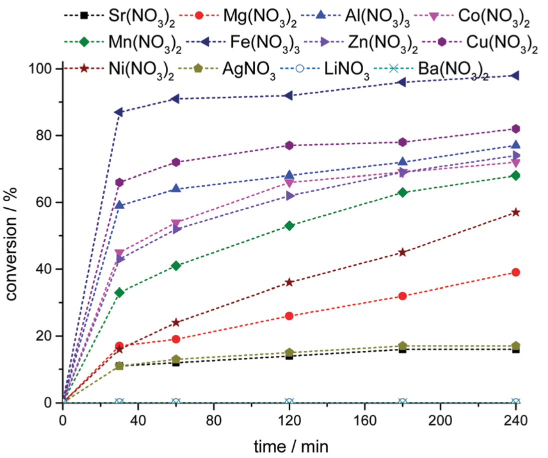
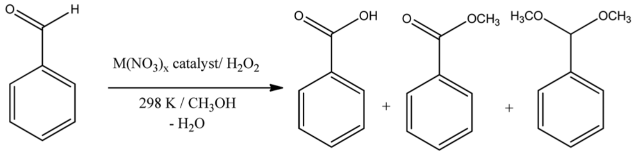


Fig. 1 Metal nitrate-catalyzed oxidative esterification of benzaldehyde with H_2O_2 in CH_3OH solutions. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (10.0 mol%), toluene (0.1 mL), CH_3OH (10.0 mL), 298 K.



Scheme 1 $M(NO_3)_3$-Catalyzed oxidative esterification of benzaldehyde with hydrogen peroxide in methyl alcohol solutions.

methyl alcohol led to the formation of benzaldehyde acetal) (Scheme 1).

Nitrate salts of cations belonging to the earlier transition metal series and to the main group of the periodic table (*i.e.*, I, II, and XIII) were evaluated. Among the first group, Fe(III) and Cu(II) nitrates were the most efficient catalysts, while Al(III) nitrate was the most efficient in the second group. Alkaline and alkaline earth metal cations were less efficient in the benzaldehyde oxidation reaction. Although $Mg(NO_3)_2$ achieved a conversion near 40%, no oxidation product was detected, only the acetal.

When we focused on the conversion and reaction selectivity, we verified that apparently a high Lewis acidity is a key aspect for both oxidation and esterification reactions (Fig. 2). The reactions that achieved higher conversion and that provided greater ester selectivity were those carried out in the presence of typical Lewis acid metal cations (*i.e.*, Fe(III), Cu(II) and Al(III) cations).[34]

Using pH measurements as a useful tool to investigate the effects of Lewis and Brønsted acidity of metal nitrate catalysts

There are several ways to estimate the Lewis acidity, for instance, by using the traditional techniques of ^{31}P NMR or infrared spectroscopy with probe molecules such as triphenylphosphine oxide or pyridine, respectively,[35,36] or new methods where fluorescence spectroscopy is the main tool.[36]

Different from Brønsted acidity, which is easily measured in solution considering the amount of H^+ ions present, the measurement of Lewis acidity requires sometimes a greater effort.[37] Nonetheless, in this case, as the reactions were carried out in alcoholic solutions, we envisage that the same method could be used to estimate the Lewis acidity. The Lewis acidity of a metal cation is strictly associated with its ability to react with a protic solvent releasing H^+ ions, which are easily detected by a glass electrode. Therefore, before the addition of oxidant, we measured the pH of the solutions containing the metal nitrate dissolved in methyl alcohol and correlated it with the reaction conversion (Fig. 2). This approach was previously used by us in other works.[38–40] It is important to highlight that although this procedure was not technically validated by any international association such as ASTM or the like, it was useful to correlate the activity of catalysts with pH measurements.

Although the expression ''pH'' should be preferentially used for aqueous acid solutions (*i.e.*, H_3O^+ ions), herein it was successfully used to quantify the H^+ ions produced by the reaction of a metal cation and a protic solvent (*i.e.*, methyl alcohol).

Fig. 3 shows that the reactions with the most acidic solutions (*i.e.*, $Fe(NO_3)_3$, $Cu(NO_3)_2$, and $Al(NO_3)_3$) were those in which higher benzaldehyde conversion and ester selectivity were achieved. These results agree with the literature, which describes that acidic catalysts are efficient to promote esterification or acetalization reactions.[41] However, it is essential to understand how the metal cations activated oxidant/substrate molecules to lead to the formation of the oxidized products.

Discussions on the reaction mechanism involving metal catalysts and hydrogen peroxide

The metal-catalyzed oxidation reactions with hydrogen peroxide can be distinguished by two mechanisms: those that may involve peroxometal or oxometal intermediates.[42] In the first case (*i.e.*, peroxometal pathway), the oxidation number of the metal cation remains unaltered along the catalytic cycle. Moreover, no stoichiometric oxidation of the substrate by the metal ion occurs.

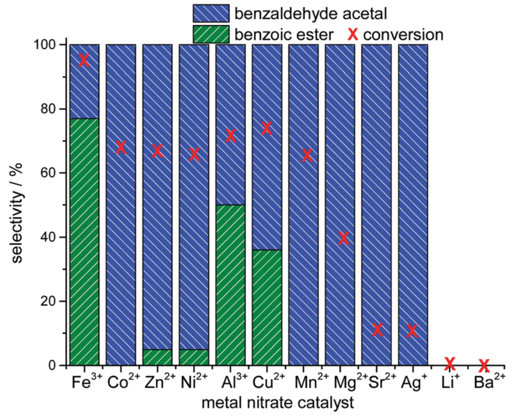


Fig. 2 Conversion and selectivity of metal nitrate-catalyzed oxidative esterification of benzaldehyde with H_2O_2 in CH_3OH solutions. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (10.0 mol%), toluene (0.1 mL), CH_3OH (10.0 mL), 298 K.

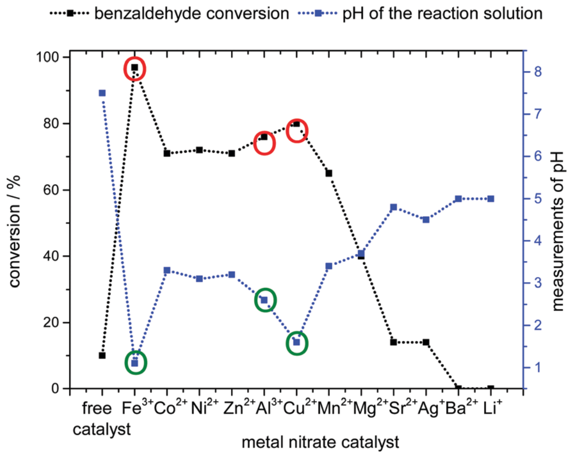


Fig. 3 Conversion and pH measurements of metal nitrate-catalyzed oxidative esterification of benzaldehyde with H_2O_2 in CH_3OH solutions. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (10.0 mol%), toluene (0.1 mL), CH_3OH (10.0 mL), 298 K.

It is very frequent when transition metals with d^0 configuration orbitals are the catalysts, which are weak oxidants (*i.e.*, Mo^{6+}, W^{6+}, Re^{7+}, Ti^{4+} ions). Conversely, in the oxometal pathway, there is variation in the oxidation number of metal catalysts, which are normally strong oxidants (*i.e.*, Cr^{6+}, Mn^{7+}, Os^{8+}) and may oxidize the substrate even in the absence of peroxide.[43]

In the present study, the cations of the metal catalysts have a low oxidation state, and the reaction may proceed through the other route; hydrogen peroxide can react with a metal cation, leading to the peroxometal intermediate. It can occur when a M^{n+}/M^{n+1} redox pair is involved.[44] The metal cation can enhance the oxidizing character of the peroxo-species acting as a Lewis acid due to the electron-withdrawing effect and promote the transfer of the oxygen atom to the substrate more efficiently.

Considering the literature and the experimental data, we have proposed a reaction pathway where both Lewis and Brønsted acids are found to be effective in converting benzaldehyde to benzoic acid. We suppose that M^+ ions may have reacted with hydrogen peroxide in the presence of alcohol, generating H^+ ions and MOOH (eqn (1), Scheme 2).

The alcohol plays an essential role in this step, providing the H^+ ion. No metal alkoxide is formed because a proton of hydrogen peroxide regenerates the alcohol. Although it could be possible for the metal nitrate catalyst to react with the aqueous hydrogen peroxide solution and release H^+ ions, apparently, under these reaction conditions, this does not happen. To support this hypothesis, we carried out a comparison of pH measurements before and after the addition of the oxidant (Fig. 4).[37]

In most of the solutions, the addition of aqueous hydrogen peroxide triggered an increase of the pH value. It may be attributed to the reaction of metal catalyst with hydrogen peroxide which leads to the hydroxyl species.[45] Nonetheless, in the case of the more active metal nitrate catalysts, this effect was absent (*i.e.*, Fe^{3+} and Cu^{2+} ions) or minimum (*i.e.*, Al^{3+} ions).

Therefore, we suggest that the reaction of metal cations (*i.e.*, Fe^{3+}, Cu^{2+}, and Al^{3+} ions) with methyl alcohol provides H^+ ions, which are essential for both oxidation and esterification reactions. In eqn (2) (Scheme 2), we suppose that MOOH species may promote the transfer of an oxygen atom to benzaldehyde resulting in benzoic acid. It has been described that Fe(III) cations can react with hydrogen peroxide forming intermediates such as MOOH. The literature has reported that iron and copper nanoparticle catalysts are efficient in the oxidation of *para*-substituted-benzaldehydes.[46] The presence of an active metal cation catalyst is the key in this step. Herein, in the absence of an efficient metal catalyst, the oxidation reaction practically did not occur, as demonstrated by the uncatalyzed reactions. Moreover, the presence of H^+ ions provides the correct stoichiometry so that this reaction occurs releasing water.

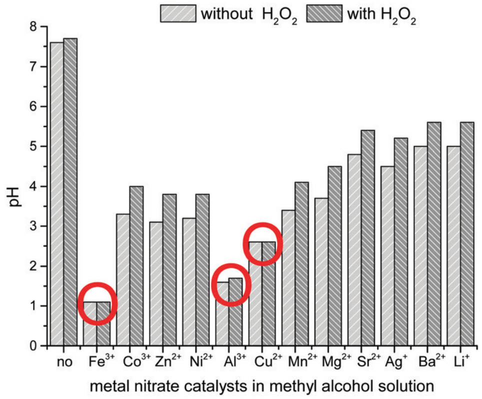
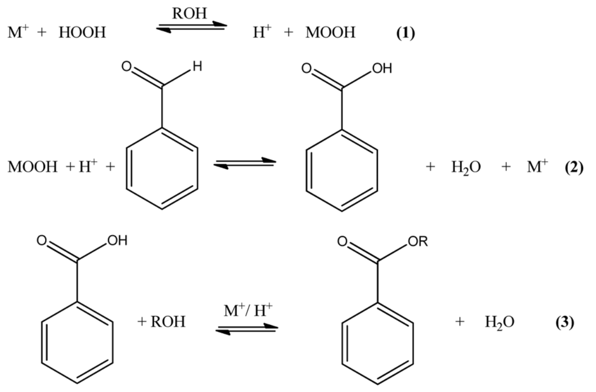


Fig. 4 Impact of hydrogen peroxide addition on the pH of the methanolic solutions containing benzaldehyde and the metal nitrate catalyst.[a] Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (10.0 mol%), toluene (0.1 mL), CH_3OH (10.0 mL), 298 K.



Scheme 2 Probable route for Lewis and Brønsted acid-catalyzed oxidative esterification of benzaldehyde.

Nonetheless, it is important to highlight that it is not the only reaction pathway possible; for instance, Thakur *et al.* proposed that the methyl ester of aromatic aldehydes can be directly obtained in the presence of titania-supported vanadium acetate without the acid formation.[23] However, as will be demonstrated in the next sections benzoic acid is also a product formed herein.

An important point is that when we added the metal nitrate to the "pure" hydrogen peroxide aqueous solution (*i.e.*, in the absence of alcohol), a violent decomposition reaction was immediately noticed, due to the collapse of hydrogen peroxide, which led to a quick evolution of molecular oxygen. Nonetheless, it is noteworthy to highlight that in the reaction solutions (*i.e.*, benzaldehyde/CH_3OH/metal nitrate) no gas release was observed.

After the formation of benzoic acid, it was almost instantaneously esterified to methyl benzoate. In GC analyses, only traces of benzoic acid were detected. Typically, esterification reactions are catalyzed by Lewis or Brønsted acids.[47–49] In eqn (3) (Scheme 2), we have described that the M^+ cation in the presence of alcohol may provide H^+ ions, which can protonate the carbonyl group of benzoic acid, facilitating its nucleophilic attack by alcohol, generating ester and water.[50]

Assessment of the nature of the iron salt catalyst

Other iron salts were investigated in benzaldehyde oxidation reaction (Fig. 5). An equal load of iron was used in all the runs. Except for ferric sulfate, all were soluble in methyl alcohol. Possibly, this was the reason for the lowest efficiency of the $Fe_2(SO_4)_3$ catalyst.

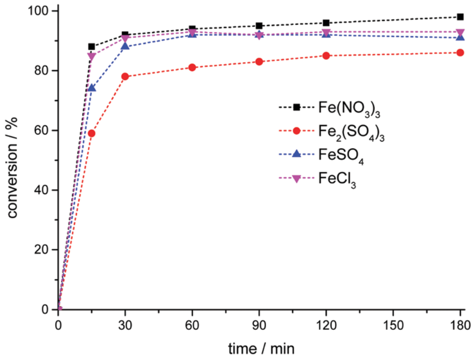


Fig. 5 Effects of the type of anion and oxidation number of the cation on iron-catalyzed oxidative esterification of benzaldehyde with H_2O_2 in CH_3OH solutions. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (2.5 mol% of Fe^{2+} or Fe^{3+} ions), toluene (0.1 mL), CH_3OH (10.0 mL), 298 K.

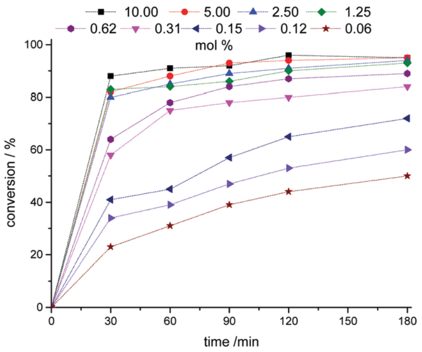


Fig. 7 Effect of the catalyst load on the conversion of benzaldehyde in $Fe(NO_3)_3$-catalyzed reactions with hydrogen peroxide. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), CH_3OH (10 mL), temperature (298 K), reaction volume (10 mL).

The reaction rate followed the trend $Fe(NO_3)_3 > FeCl_3 > FeSO_4 > Fe_2(SO_4)_3$ (Fig. 5). Even when using the same iron load, the reactions presented different conversions and selectivity. Once again, we may suppose that there is a correlation between the ester selectivity and the pH of solutions after the addition of iron salts (Fig. 6).

The reactions carried out in more acidic solutions were those that achieved higher conversion and ester selectivity. The oxidation state was also important; among the totally soluble catalysts, ferrous sulfate was the lowest effective.

When the catalyst was less efficient, acetal was the major product; conversely, ester was the most selective product when the iron catalyst was acidic enough to lead the pH value to a level lower than 2.0.

Impact of $Fe(NO_3)_3$ catalyst load on benzaldehyde oxidation by H_2O_2 in CH_3OH

The effect of catalyst load was assessed in a wide range of values (*ca.* 0.06 to 10.0 mol%, Fig. 7). Within the concentration interval of 10.0 to 1.25 mol%, regardless of the catalyst load, all the reactions had a maximum conversion after a 3 h reaction. Below this range, a decrease in catalyst load resulted in a concomitant decrease in both rate and reaction conversion. The maximum TON achieved was 900, with 54% of conversion using 0.06 mol% of catalyst, indicating a high activity at room temperature.

On the other hand, the selectivity of reactions was more sensitive to variation of the catalyst load (Fig. 8). The catalyst concentration was crucial for ester formation; it was the major product only until 1.25 mol%, with a high conversion (*ca.* 95%). Below this load, benzaldehyde acetal became the main product.

Indeed, at the lowest concentration (*ca.* 0.06 mol%), despite the conversion of 50%, no ester was detected. This suggests that under these conditions, condensation of benzaldehyde with methyl alcohol, which is also an acid-catalyzed competitive reaction, occurs more favorably than esterification and oxidation reactions.

Scheme 2 describes the possible participation of both Lewis (*i.e.*, M^+ ions) and Brønsted (*i.e.*, H^+ ions) catalysts in the oxidative esterification reaction. We can note that the oxidation depends on the presence of active species MOOH. Therefore,

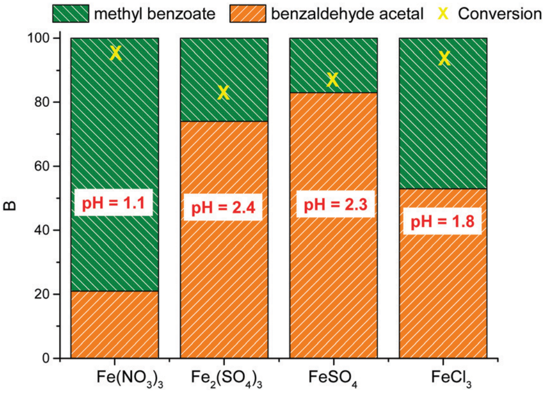


Fig. 6 Effects of the type of anion and oxidation number of cations on the conversion, selectivity, and pH value of oxidative esterification reactions of benzaldehyde with H_2O_2 in CH_3OH solutions. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (2.5 mol% of Fe^{2+} or Fe^{3+} ions), toluene (0.1 mL), CH_3OH (10.0 mL), 298 K.

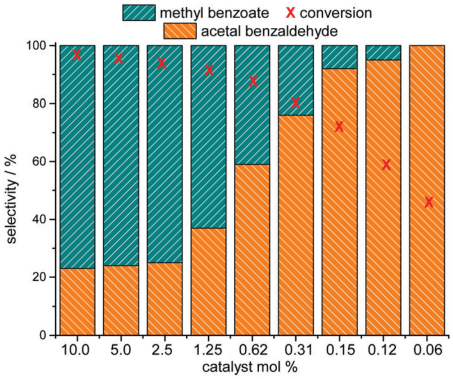


Fig. 8 Influence of the catalyst load on the conversion and selectivity of metal nitrate-catalyzed oxidative esterification of benzaldehyde with H_2O_2 in CH_3OH solutions. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (variable), CH_3OH (10.0 mL), 298 K.

the decrease in the selectivity of oxidation products is a consequence of the decrease of metal catalyst load. On the other hand, the acetalization reaction which is the concurrent reaction was less impacted by the reduction of the catalyst load. Possibly, the significant excess of alcohol in solution was advantageous toward the acetal formation reaction.

Different from the selectivity, the catalyst load has no effect on the reaction equilibrium and therefore it should not affect the conversions. Nonetheless, since they did not reach equilibrium, we verified that the reaction conversions were also impacted by the catalyst load. Within the period studied, the conversions were lower when the catalyst load was lower than 1.25 mol%. It can be assigned to the lower H^+ amount generated in the solution, which depends on the metal catalyst load.

Effects of molar ratio of the oxidant to substrate

The oxidant load played a key role in $Fe(NO_3)_3$-catalyzed benzaldehyde oxidation with H_2O_2 in CH_3OH solutions. Fig. 9 and 10 display the main data of conversion and selectivity obtained in reactions with different amounts of oxidant.

An excess of oxidant was detrimental for both rate and reaction conversion. This can be assigned to the reversible character of the esterification reaction, which gives water as a co-product. Nonetheless, the ester selectivity was higher when a higher oxidant load was used (Fig. 10).

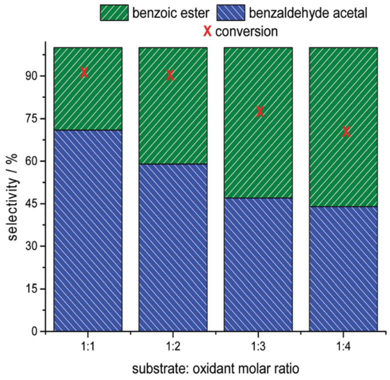


Fig. 10 Effect of oxidant load on the conversion and selectivity of $Fe(NO_3)_3$-catalyzed oxidative esterification reactions of benzaldehyde with H_2O_2. Reaction conditions: benzaldehyde (10 mmol), $Fe(NO_3)_3$ catalyst (0.625 mol%), CH_3OH (163 mmol), temperature (298 K), reaction volume (10 mL).

Effect of alcohol on the $Fe(NO_3)_3$-catalyzed oxidative esterification of benzaldehyde

When the hydroxyl groups are sterically hindered the reactivity of alcohols is affected. It may be a key aspect for both esterification and acetalization reactions. Therefore, to assess this effect various alcohols were evaluated in reactions with hydrogen peroxide and benzaldehyde in the presence of $Fe(NO_3)_3$ as a catalyst (Fig. 11).

Alcohols with a greater carbon chain size and with a high steric hindrance were less reactive (*i.e.*, primary > secondary > tertiary) (Fig. 11). The more hindered the hydroxyl group of the alcohol, the more difficult the attack of the carbonyl carbon of benzaldehyde, and consequently, the lower the ester selectivity (Scheme 3).

Similarly, when alcohols with a carbon chain size greater than that of ethyl alcohol are used, the approximation of carbonyl carbon becomes less favorable. The following tendency was observed in terms of conversion of alcohols; $CH_3OH > C_2H_5OH > C_3H_7OH > C_4H_9OH >$ iso-$C_4H_9OH >$ iso-$C_3H_7OH >$ *sec*-$C_4H_7OH >$ *tert*-C_4H_9OH. Truly, the reaction selectivity was strongly impacted by alcohol's nature. An increase in carbon chain size affected the selectivity of esters (Scheme 3). For linear primary alcohols, it was verified. The same occurred for secondary alcohols. Particularly, for C_4-alcohols, the ester selectivity was *n*-butyl > iso-butyl > *sec*-butyl > *tert*-butyl (Scheme 3). Moreover, acetalization reactions were also impacted, mainly by the size of the carbon chain of alcohol. Acetal and hemiacetal were the expected products; nonetheless, depending on the type of alcohol, only one of them was selectively formed (Scheme 4).

We have found that only alcohols with shorter carbon chain size efficiently acetalized benzaldehyde (*i.e.*, CH_3OH and C_2H_5OH);

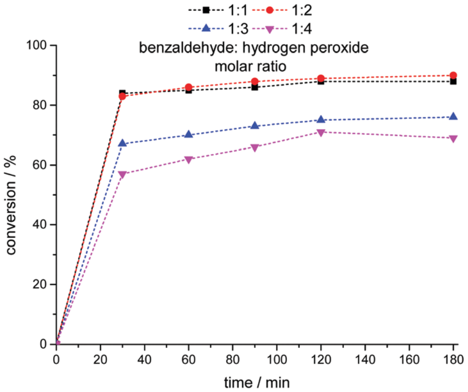


Fig. 9 Impact of oxidant load on the conversion of benzaldehyde in $Fe(NO_3)_3$-catalyzed reactions with hydrogen peroxide. Reaction conditions: benzaldehyde (10 mmol), $Fe(NO_3)_3$ catalyst (0.625 mol%), CH_3OH (10 mL), temperature (298 K).

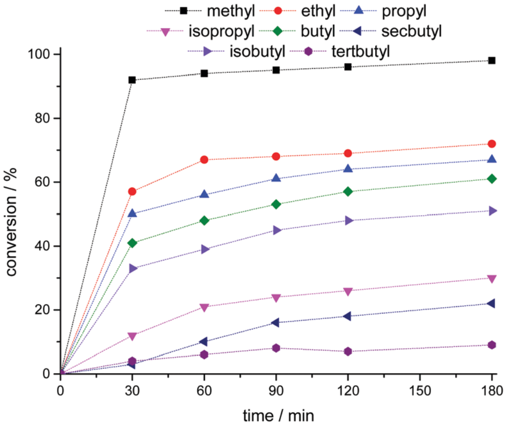
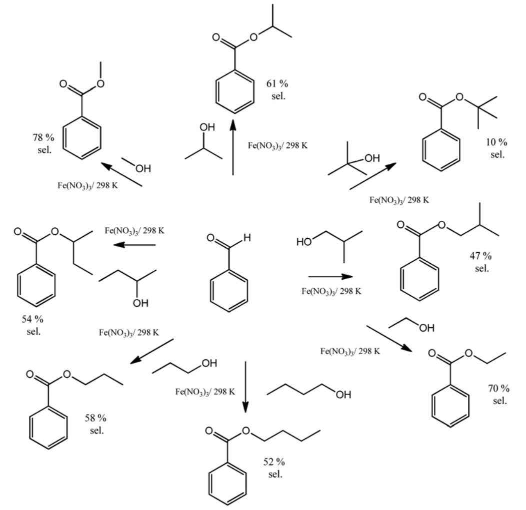
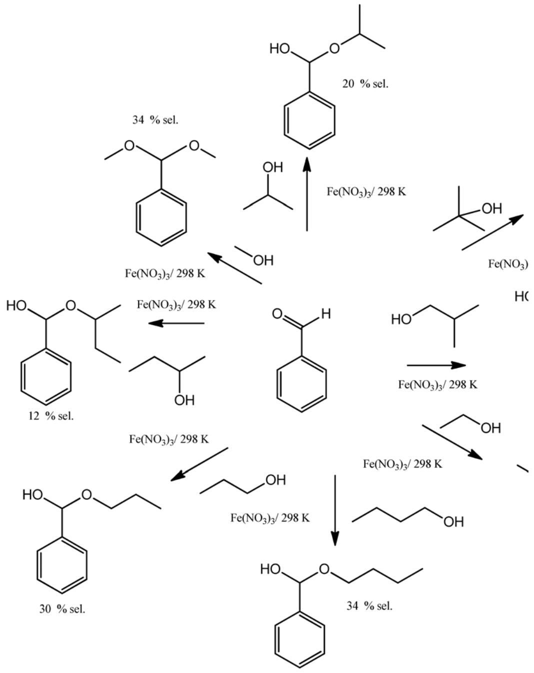


Fig. 11 Effect of the alcohol on the conversion of benzaldehyde in $Fe(NO_3)_3$-catalyzed reactions with hydrogen peroxide. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), catalyst (2.5 mol%), temperature (298 K), reaction volume (10 mL).



Scheme 3 Ester selectivity of $Fe(NO_3)_3$-catalyzed oxidative esterification reactions of benzaldehyde with hydrogen peroxide in alcoholic solutions. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), $Fe(NO_3)_3$ catalyst (2.5 mol %), temperature (298 K), reaction volume (10 mL).



Scheme 4 Acetal and hemiacetal selectivity of $Fe(NO_3)_3$-catalyzed benzaldehyde reactions with alkyl alcohol in the presence of hydrogen peroxide. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), $Fe(NO_3)_3$ catalyst (2.5 mol%), temperature (298 K), reaction volume (10 mL).

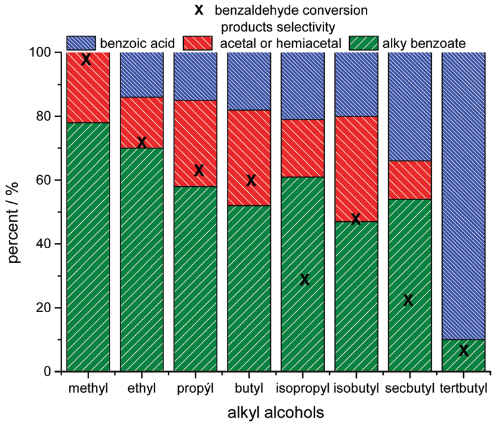


Fig. 12 Effect of the alcohol on the conversion and selectivity of benzaldehyde in $Fe(NO_3)_3$-catalyzed reactions with hydrogen peroxide. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), $Fe(NO_3)_3$ catalyst (2.5 mol%), temperature (298 K), reaction volume (10 mL).

in the reactions with other alcohols, hemiacetal was the condensation product formed. This can be assigned to the steric hindrance of the hydroxyl group of secondary and tertiary alcohols as well as a longer carbon chain.

Another important change occurred when the reactivity of the alcohols in esterification and acetalization reactions was diminished; benzoic acid began to be formed in detectable amounts. Only in the reaction with methyl alcohol, it was not verified. For better visualization of the product distribution, as well as the final conversion of benzaldehyde, these data are summarized in Fig. 12.

In all the reactions, except for *tert*-butyl alcohol, ester was the most selective product. However, the formation of hemiacetal or acid depended on the type of alcohol.

The values of pH were also measured in the reactions with different alcohols. The following values were obtained: methyl alcohol (1.1); ethyl alcohol (1.5); propyl alcohol (1.6); isopropyl alcohol (1.7); butyl alcohol (1.7); isobutyl alcohol (1.7). In addition to the effects of the size of the carbon chain and steric hindrance on the hydroxyl group, we suppose that the pH of the alcoholic solution was also important to explain the decrease in the conversion of reactions; with an increase in pH values, the reaction became less favorable.

Effect of temperature on the $Fe(NO_3)_3$-catalyzed oxidative esterification of benzaldehyde

The impact of temperature on conversion and selectivity was also investigated (Fig. 13). It is an expected effect, since an increase in temperature means a higher amount of energy is provided to the reactant molecules and consequently an increase in the number of effective collisions.

Ethyl alcohol was selected aiming at a greater temperature interval reaction, and consequently, the number of effective collisions was also increased, improving the reaction rate. An increase in reaction temperature resulted in a higher conversion of benzaldehyde.

Nonetheless, herein the reactions were less sensitive to the increase in temperature; the difference between the conversions achieved at the highest and lowest levels of temperature was small. Even though the catalyst load was also varied, the gap between the conversions was not large enough in that the reactions carried out at the intermediate temperatures between these two levels could not be efficiently measured (Fig. 13).

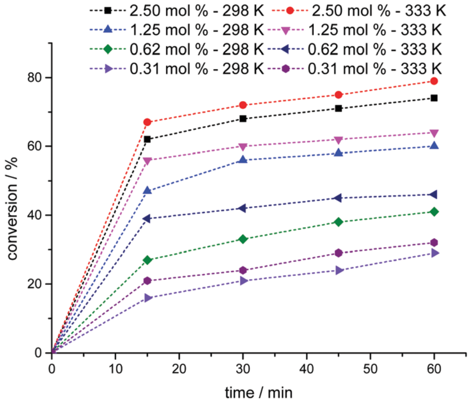


Fig. 13 Effects of temperature and catalyst load on the conversion of $Fe(NO_3)_3$-catalyzed oxidative esterification reactions of benzaldehyde by H_2O_2. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), $Fe(NO_3)_3$ catalyst (variable), temperature (variable), ethyl alcohol volume (10 mL).

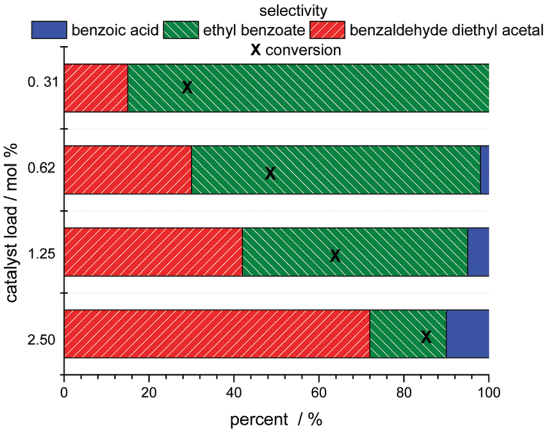


Fig. 14 Effect of the catalyst load on the conversion and selectivity of $Fe(NO_3)_3$-catalyzed oxidative esterification reactions of benzaldehyde with hydrogen peroxide in ethyl alcohol solutions. Reaction conditions: benzaldehyde (1.0 mmol), H_2O_2 (2.0 mmol), $Fe(NO_3)_3$ catalyst (variable), temperature (333 K), reaction volume (10 mL).

To circumvent this obstacle, the reactions should be carried out using a lower alcohol excess; nonetheless, it is out of the scope of this study, because the main reaction (*i.e.*, oxidative esterification) will be compromised.

Under these reaction conditions, no significant difference was found in the reactions carried out at the lowest (*ca.* 298 K) and highest temperature (*ca.* 333 K). Thus, only data obtained at 333 K were presented (Fig. 14).

As verified in the oxidation reactions of benzaldehyde in methyl alcohol solutions at 298 K (Fig. 8), a decrease in catalyst load reduced both conversion and ester selectivity. Conversely, diethyl benzaldehyde acetal had its selectivity enhanced in reactions with a lower catalyst load.

Conclusions

A green route to oxidatively esterify benzaldehyde at room temperature in a one pot-reaction with an environmentally friendly oxidant (*i.e.*, aqueous H_2O_2) using an inexpensive commercial Lewis acid catalyst (*i.e.*, $Fe(NO_3)_3$) in alcoholic solutions was developed. Among the several metal nitrate salts assessed, $Fe(NO_3)_3$ was the most active catalyst. The main aspects that drive the reaction selectivity were studied. Benzoic acid and alkyl ester were obtained in a one-pot process. Methyl and ethyl alcohols were efficiently converted to esters (*ca.* 72–75% selectivity), in 1 h of reaction at 298 K with a low oxidant excess (*ca.* 1 : 2). In this case, acetal was a secondary product. When the reaction scope was extended to the other alcohols, the formation of two side-products was noticed: benzoic acid and hemiacetal. Depending on the reaction conditions (*i.e.*, catalyst and oxidant loads), alkyl benzoate or hemiacetal(acetal) benzaldehyde were the main products. Secondary alcohols with a carbon chain size greater than that of ethyl alcohol provided hemiacetal as the co-product and lower ester selectivity. The high activity of the $Fe(NO_3)_3$ catalyst may be assigned to its higher Lewis acidity strength. After performing the pH measurements before and after adding the oxidant to the reaction medium, we concluded that the most efficient catalysts were those that led to a higher decrease in pH values ($Fe(NO_3)_3 > Cu(NO_3)_2Al(NO_3)_3$). Noticeably, we demonstrated that these metal nitrate catalysts promoted the oxidation reactions reacting with both solvent and oxidant. It is noteworthy that this methodology does not rely upon ligands and other additives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the Federal University of Viçosa, the PPGMQ-MG, and the development agencies CNPq and FAPEMIG. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

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