



Bismuth ferrite (BiFeO_3) nanopowder prepared by sucrose-assisted combustion method: A novel and reusable heterogeneous catalyst for acetylation of amines, alcohols and phenols under solvent-free conditions

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ABSTRACT

Bismuth ferrite (BiFeO_3) nanopowder was prepared by the novel combustion technique using sucrose as a fuel. The catalyst was characterized by using XRD, FT-IR, scanning electron microscope (SEM), transmission electron microscope (TEM), and BET surface area measurement and used as the heterogeneous catalyst for the acetylation reaction under solvent-free conditions. Efficient and selective acetylation of various amines, alcohols and phenols was carried out over BiFeO_3 nanopowder by using acetic anhydride and/or acetyl chloride as the acetylating agents at room temperature under solvent-free conditions. The method is highly chemoselective – alcoholic hydroxyl group can be protected while phenolic hydroxyl group remains intact and the amine group can be acetylated in the presence of hydroxyl. This method is fast, high yielding, clean, safe, cost effective, compatible with the substrates having other functional groups and very suitable for practical organic synthesis. The catalyst can also be reused for acetylation without loss of catalytic activity.

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1. Introduction

The acylation of alcohols, phenols and amines is one of the most useful and versatile transformations in organic synthesis [1]. Among them, the conversion of hydroxyl or amino group into the corresponding acetate or acetamide is essential due to its medicinal value, e.g. the preparation of paracetamol from 4-aminophenol as well as for confirmation of the presence of hydroxyl or amino group in a compound. In addition, the protection of hydroxyl functionality as acetate is preferred due to its ease of introduction, stability under mild acidic reaction conditions and ease of removal by mild alkaline hydrolysis. The acetylation of alcohols and phenols or amines is usually performed with acetic anhydride or acetyl chloride in the presence of bases such as triethylamine, pyridine, 4-(dimethylamino)pyridine (DMAP), 4-pyrrolidinopyridine and tributylphosphine [2,3]. In the literature, several methods have been developed for the preparation of acetate from the corresponding alcohol, phenol or thiol using various Lewis acid catalysts such as CoCl_2 [4], ZnCl_2 [5], TaCl_5 [6], InCl_3 [7], RuCl_3 [8], $\text{TiCl}_4\text{-AgClO}_4$ [9], LiClO_4 [10], $\text{Mg}(\text{ClO}_4)_2$ [11], $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ [12], $\text{Sc}(\text{OTf})_3$ [13], $\text{Sc}(\text{NTf}_2)_3$ [14], Me_3SiOTf [15], $\text{In}(\text{OTf})_3$ [16], $\text{Cu}(\text{OTf})_2$ [17], $\text{Ce}(\text{OTf})_3$ [18], $\text{Bi}(\text{OTf})_3$ [19] and I_2 [20]. However,

some of these protocols are associated with one or more drawbacks; use of hazardous materials, use of excess acetylating agent, use of expensive and moisture sensitive catalysts such as metal triflates and perchlorates, intolerance of other functional groups, tedious preparation of catalysts, harsh reaction conditions, utilization of halogenated volatile organic solvents, and poor yields of the desired products.

In order to overcome the above problems and owing to the growing environmental considerations, development of green processes using heterogeneous catalysts under solvent-free conditions has aroused great interest in recent years [21]. Heterogeneous catalysts are more advantageous over homogeneous catalysts as they can be easily recovered from reaction mixture by simple filtration and can be reused several times, making the process more economically and environmentally viable. In this context, heterogeneous catalysts such as yttria-zirconia-based catalysts [22], metal oxides such as ZnO , CuO , NiO , CoO , Mn_2O_3 , Cr_2O_3 [23], montmorillonites [24], $\text{HClO}_4\text{-SiO}_2$ [25], $\text{H}_2\text{SO}_4\text{-SiO}_2$ [26], $\text{AlPW}_{12}\text{O}_{40}$ [27], zeolites [28], Nafion-H [29], $\text{HBF}_4\text{-SiO}_2$ [30], $\text{KF-Al}_2\text{O}_3$ [31], silica embedded-triflate catalysts [32], Cp_2ZrCl_2 [33], $\text{H}_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}$ [34], $\text{MoO}_3\text{-Al}_2\text{O}_3$ [35], $\text{NaHSO}_4\text{-SiO}_2$ [36], $\text{Sn}(\text{TPP})(\text{BF}_4)_2$ [37], sulphated zirconia [38] and $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ [39] have been utilized to achieve the acetylation of alcohols, phenols, thiols, and amines. However, there is always the need for better methodology for this type of widely used reaction.

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Perovskite-type mixed oxides (ABO_3) are one of the most important inorganic solids which have been extensively used as heterogeneous catalysts for many industrial reactions, including hydrocarbon oxidation [40], NO_x decomposition [41], and oxidation of CO [42] and NH_3 [43]. Perovskite mixed oxides are characterized by high resistance to dissolution in aqueous and non-aqueous solvents, and also in acidic and basic fluids. These properties make them suitable heterogeneous catalysts for the organic transformations. However, to the best of our knowledge, there is no report that these mixed oxides were used for catalytic acetylation of functional groups.

In this work, we report on the preparation of perovskite-type bismuth ferrite ($BiFeO_3$) nanopowder by sucrose-assisted combustion synthesis and its application as a heterogeneous catalyst for efficient acetylation of alcohols, phenols and amines under solvent-free conditions.

2. Experimental

2.1. Catalyst preparation

Bismuth ferrite was prepared by a novel combustion method using sucrose as the fuel. The precursor was prepared in aqueous solution from metal nitrates and sucrose, at molar ratio of $Bi(III):Fe(III):sucrose = 1:1:2$ as follows. To a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (10 mmol) in 10 mL of distilled water was added $Bi(NO_3)_3 \cdot 5H_2O$ (10 mmol) dissolved in 10 mL of 3 M nitric acid solution. The appropriate amount of sucrose (20 mmol) was then added to the above solution and the mixture was stirred until complete dissolution occurred. Then, the mixture was heated and evaporated at $100^\circ C$ on a hot plate with stirring till it become a dark viscous resin. Continuous heating leads to the auto-ignition of dried resin with the evolution of large quantities of gases. The brownish color ash obtained after combustion was analyzed for perovskite-type $BiFeO_3$ phase. The whole process was over after 30 min, but the time between the actual ignition and the end of the reaction was less than 20 s.

The crystal structure of the synthesized powder was characterized by a Bruker D8 Advance X-ray diffractometer using $Cu K\alpha$ radiation ($\lambda = 0.15405$ nm). Infrared spectra were recorded on a Shimadzu system FT-IR 8400 spectrophotometer using the KBr pellet method. The morphology of powder was revealed by a scanning electron microscope (SEM, Philips XL-30) and a transmission electron microscope (TEM, LEO-906E). The TEM image of product was obtained at the accelerating voltage of 200 kV. TEM samples were prepared by dropping the ethanol dispersion on a carbon-coated copper grid. Specific surface area was calculated by the BET method using nitrogen.

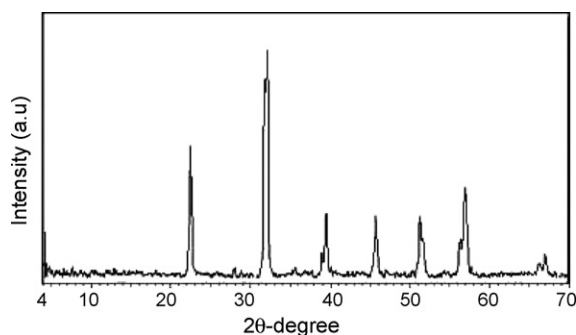


Fig. 1. XRD pattern of $BiFeO_3$ nanopowder.

2.2. General experimental procedure

To a mixture of $BiFeO_3$ nanopowder (100 mg) and acetic anhydride or acetyl chloride (1 mmol), amine, alcohol or phenol (1 mmol) was added. The reaction mixture was stirred for the required period of time at room temperature. The progress of the reaction was followed by TLC or GC. After completion of the reaction, the product was extracted with CH_2Cl_2 and filtered to remove $BiFeO_3$. The organic phase was treated with saturated bicarbonate solution and dried over anhydrous sodium sulphate. The solvent was removed under vacuum to afford the pure product (Tables 2–4). The products are characterized on the basis of 1H NMR and GC-MS.

2.3. Recycling of the catalyst

At the end of the acetylation of aniline, the catalyst was filtered, washed with dichloromethane, dried and activated at $200^\circ C$ for 1 h, and reused in another reaction (Table 5).

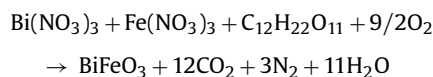
3. Results and discussion

3.1. Characterization of $BiFeO_3$ nanopowder prepared by sucrose combustion method

Among the various wet chemical processes, the combustion route is found to be simple and cost effective for the synthesis of homogeneous, very fine, crystalline nanopowders without the intermediate decomposition and/or calcination steps which other conventional synthesis routes would require. The process is based on the mixing of reactants that oxidize easily, such as metal nitrates, and an organic fuel, acting as a reducing agent. An external heat supply is needed to initiate the ignition of the mixture leading to a self-sustainment of an exothermic redox reaction.

Physicochemical properties of the oxide powders synthesized by combustion processes mainly depend on the nature and amount of fuel used. In order to identify the suitable fuel for the synthesis of $BiFeO_3$, we tested various organic fuels such as urea, citric acid, glycine and sucrose. Among them, we found that sucrose ($C_{12}H_{22}O_{11}$) is the best fuel and resulted in the formation of pure and nano-size $BiFeO_3$ powder. As an easy-obtained agriculture product, sucrose is low-cost compared with other organic fuels.

Sucrose functioned as both complexing agent and fuel in the whole process. During the evaporation of starting solution, it was hydrolyzed in the presence of H^+ (from nitric acid) and converted into glucose and fructose, which can be further oxidized into saccharic acid, glycolic acid and trihydroxy-butyric acid with a number of $-COOH$ and $-OH$ groups. Specially, the $-COOH$ groups can easily combine with metal ions, which is quite similar to the citric acid complexing mechanism. During the combustion process, the chelating complexes decomposed and a mass of gases are generated, which are favored of the formation of very fine particles. The total combustion reaction between bismuth(III) and iron(III) nitrates and sucrose to form $BiFeO_3$ powder can be written as follows:



The XRD pattern of the as-prepared $BiFeO_3$ powder is shown in Fig. 1. This pattern showed only the peaks corresponding to perovskite-type $BiFeO_3$ (JCPDS File No. 20-169), which crystallizes in the rhombohedral system. The perovskite synthesized is in an essentially pure phase, as evidenced by its XRD. No peaks attributable to Bi_2O_3 and/or Fe_2O_3 and unreacted precursor materials were detectable. The mean particle size of $BiFeO_3$ was calculated

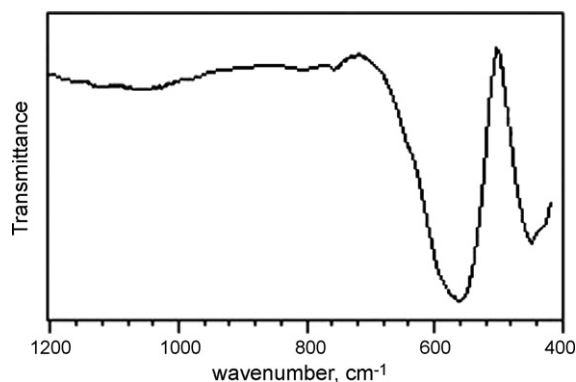


Fig. 2. FT-IR spectrum of BiFeO₃ nanopowder.

using the Scherrer equation, $D = (0.89\lambda) / (\beta_{1/2} \cos \theta)$, where λ is the wavelength for Cu K α radiation, $\beta_{1/2}$ is the corrected full width at half maximum (FWHM) and θ is the Bragg angle. The crystallite size of the powder particles is calculated at about 42 nm. This value agreed well with SEM and TEM observations (vide infra).

In the FT-IR spectrum of product, there are two strong absorptive bands at about 560 and 440 cm⁻¹ (Fig. 2). These bands correspond to Fe–O stretching and O–Fe–O bending vibrations of FeO₆ groups in perovskite BiFeO₃, respectively [44]. This finding proves the formation of the perovskite BiFeO₃ and is in accordance with the XRD data.

It is well-known that the catalytic activity of ABO₃ perovskite is strongly dependent on the shape, size and size distribution of the particles. Therefore, it is of paramount importance to characterize the microstructure of the powder obtained. Fig. 3 shows the SEM and TEM images of the product. The SEM image reveals that powder is composed of loosely aggregated extremely fine particles. From this image, it is evident that particles have a narrow nano-size distribution and homogeneous shape. TEM confirms that BiFeO₃ particles possess semi-spherical morphology and a narrow distribution of sizes in the range of 28–50 nm. Some grains are also observed on the TEM image which are composed of extremely fine particles and are essentially secondary agglomerates of primary particles.

The combustion finishes in a short heating time. Therefore, we suppose that the growth of grain size does not occur in the reaction, and very fine particles of BiFeO₃ are obtained. Large amount of gases generated in the combustion process also might prevent the particles from growing and aggregating as well. Regular distribution of nanoparticles is also attributed to the uniform temperature gradient maintained on the reaction mixture by combustion heating. The specific surface area of BiFeO₃ nanopowder measured by the BET method is 86 m² g⁻¹. This relatively high specific surface area of BiFeO₃ is beneficial to its catalytic activity.

3.2. Evaluation of catalytic activity of BiFeO₃ nanopowder for the acetylation reaction

The main objective of the work was to investigate the activity of BiFeO₃ nanopowder as the heterogeneous catalyst for the acetylation reaction. Therefore, once the perovskite-type BiFeO₃ nanopowder was characterized, it was tested as catalyst for the protection of various functional groups. To find out the activity of BiFeO₃ nanopowder as a general acetylation catalyst, we chose aniline (**1**) as a representative substrate and treated **1** with acetic anhydride under solvent-free conditions. The acetylation of **1** finished in 5 min at room temperature to give acetanilide (**2**) in 98% yield (Scheme 1).

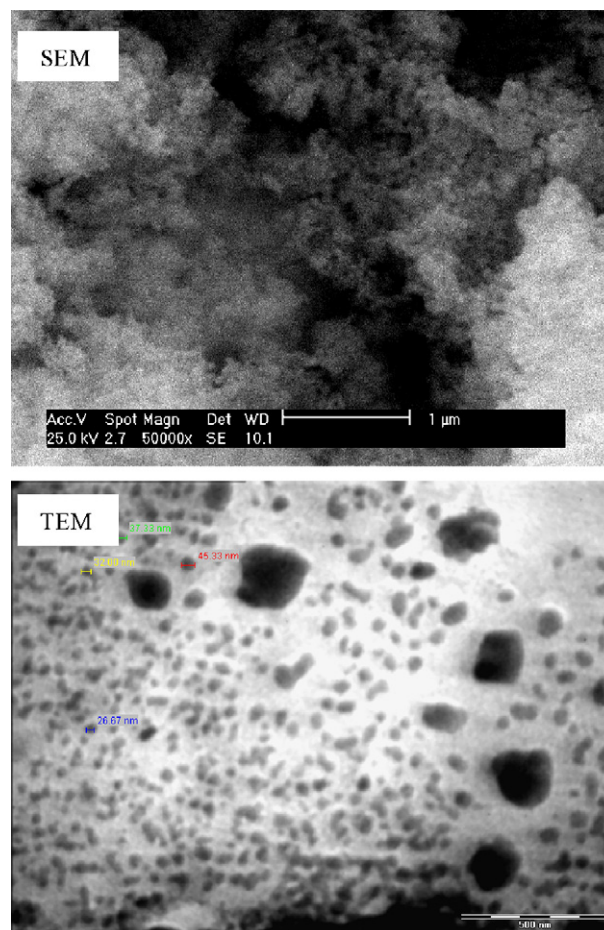
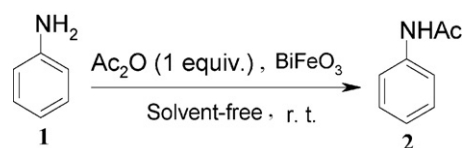


Fig. 3. SEM and TEM images of BiFeO₃ nanopowder.



Scheme 1. Acetylation of aniline over BiFeO₃ nanopowder.

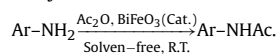
Control experiment in the absence of BiFeO₃ gave only about 20% of **2** after 30 min. On the other hand, this catalyst was not efficient in the presence of organic solvents such as acetonitrile, toluene and dichloromethane (Table 1, entries 1–3). This observation confirms that the solvent-free condition plays an important role in this acetylation reaction. So that, a rate enhancement was observed when the reaction was carried out without any solvent (Table 1, entry 4).

Table 1
Acetylation of aniline with acetic anhydride in some solvents over BiFeO₃ nanopowder^a.

Entry	Solvent	Time (min)	Yield ^b (%)
1	CH ₃ CN	120	80
2	Toluene	180	45
3	CH ₂ Cl ₂	180	70
4	Without solvent	5	98

^a Reaction conditions: aniline (1 mmol), acetic anhydride (1 mmol), catalyst (100 mg), solvent (10 mL) at rt.

^b Yields are for isolated pure acetanilide.

Table 2Acetylation of amines with acetic anhydride over BiFeO₃ nanopowder as a heterogeneous catalyst^a.

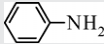
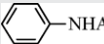
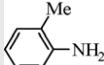
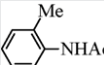
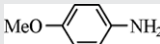

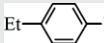
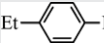

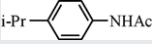
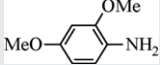
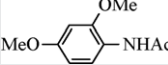
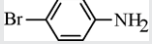
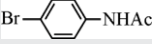
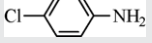
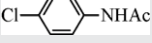
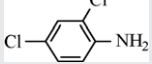
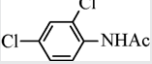
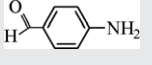
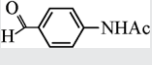
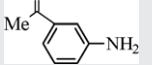
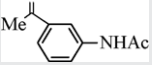
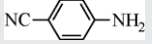
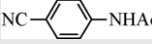
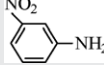
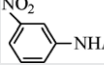
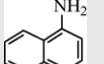
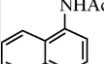
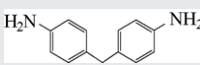
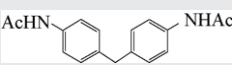
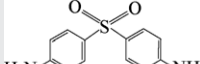
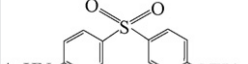
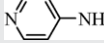
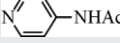
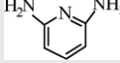
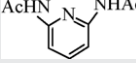
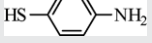
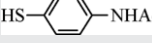

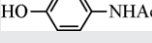
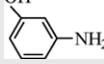
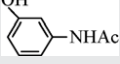
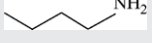
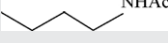
Entry	Amine	Product	Time (min)	Yield ^b (%)
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2			5	96
3			5	98
4			5	98
5			5	95
6			5	98
7			5	98
8			5	95
9			20	95
10			10	88
11			15	92
12			10	85
13			5	96
14			5	80
15			5	98
16			5	95
17			15	60
18			20	70
19			5	95
20			5	95
21			5	98
22			15	90

Table 2 (Continued)

Entry	Amine	Product	Time (min)	Yield ^b (%)
23			10	93

^a Reaction conditions: amine (1 mmol), acetic anhydride (1 equiv. per NH₂ group), catalyst (100 mg), without solvent at rt.

^b Yields are for isolated pure products.

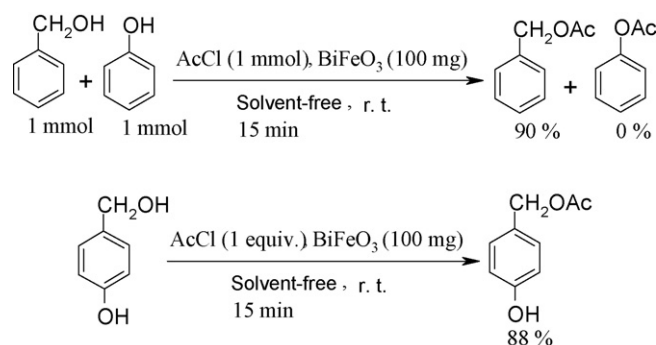
To establish the general applicability of BiFeO₃ nanopowder as an acetylation catalyst, a wide range of anilines containing various electron-donating and -withdrawing groups and primary aliphatic amines were treated with acetic anhydride (Table 2). Excellent results were obtained in each case affording the corresponding acetylated derivatives in 75–98% yields in 5–20 min at room temperature under solvent-free conditions. The excellent activity of nano-size BiFeO₃ was demonstrated by the high yields obtained for anilines having electron-withdrawing groups (Table 2, entries 10–13). Furthermore, heteroaromatic amines such as aminopyridines were converted to the corresponding acetates in good yields (Table 2, entries 17 and 18).

In contrast to primary aromatic amines which were readily acetylated by this method, secondary amines such as diphenylamine did not undergo any change. Interestingly, in a competitive acetylation reaction of an equimolar mixture of aniline and benzyl alcohol by this procedure, the amine was acetylated selectively in 96% yield within 5 min leaving the alcohol unaffected. Thus, acetylation of amino alcohols and amino phenols produced the corresponding acetamides as sole products; the hydroxyl moiety remained untouched (Table 2, entries 19–21). This selective acetylation of a primary NH₂ over a primary OH by this process is of considerable synthetic importance and is difficult to achieve with many other reagents. Aliphatic amines such as n-butylamine and also benzylamine gave the corresponding acetamides in high yields under the present reaction conditions (Table 2, entries 22 and 23). On the other hand, a variety of other functional groups such as OMe, -CHO, -COMe, -CN and -NO₂ also survived under the reaction conditions. The conversion of aniline into acetanilide on a 100 mmol scale proceeded just as well as the 1 mmol reaction (12 min, 96%).

To explore the potential of this catalytic system, we studied the acetylation of alcohols under solvent-free conditions. The acetylation with acetic anhydride was too sluggish for practical application. In order to overcome this drawback, acetyl chloride was used as an acetylating agent. In a short reaction time, the desired esters were obtained in excellent yields from the reaction of a variety of benzylic, primary, secondary and hindered tertiary alcohols (1 mmol) with acetyl chloride (1 mmol) in the presence of catalytic amount of BiFeO₃ (100 mg) (Table 3).

All primary benzylic alcohols were selectively converted to the corresponding acetates in quantitative yields without any evidence for the formation of side products (Table 3, entries 1–8). In this case, not only electron-rich benzylic substrates but also electron-deficient ones were converted to the acetate derivatives in high yield. Various secondary alcohols were converted to the corresponding acetates as well (Table 3, entries 9–14). In a controlled blank experiment, acetylation of benzyl alcohol with acetyl chloride under similar reaction conditions did not proceed in the absence of catalyst.

This acetylation protocol is also efficient for allylic systems. For example, cinnamyl alcohol was selectively converted to the corresponding acetate and the double bond remained intact under these reaction conditions (Table 3, entry 15). It is very interesting to note that sterically hindered tertiary alcohol such as triphenylmethanol can also be acetylated in moderate yield under these reaction conditions albeit with longer reaction time (Table 3, entry



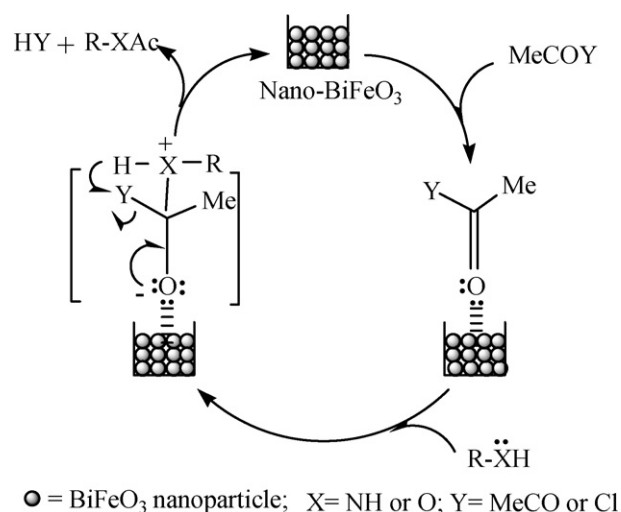
Scheme 2. Competitive acetylation between alcoholic and phenolic OH groups.

16). GC–MS analysis showed no elimination product in this reaction mixture. Non-activated aliphatic alcohols were also converted into the corresponding acetate compounds with high efficiency under the same reaction conditions (Table 3, entries 17–20). Among the various alcohols studied, primary benzylic alcohols were found to be most reactive, giving the corresponding acetylated products within shorter reaction times.

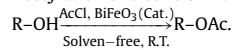
Further, we investigated inter- and intramolecular competitive acetylation of alcohols and phenols. It is found that the alcoholic OH was acetylated selectively in the presence of phenolic OH (Scheme 2).

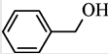
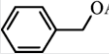
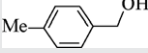
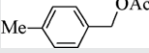
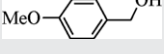
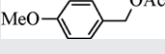
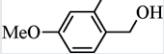
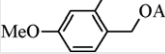
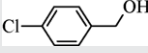
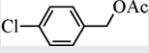
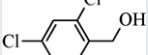
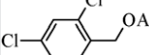
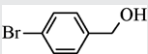
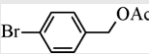
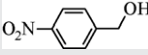
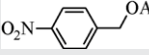
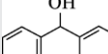
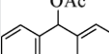
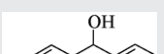
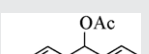
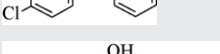
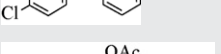
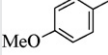
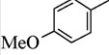
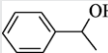
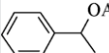
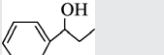
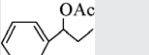
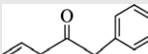
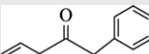
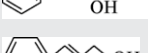
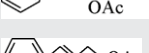
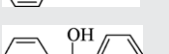
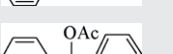
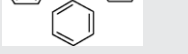
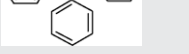


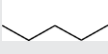

To evaluate the scope of this protocol, the acetylation of phenols was also investigated. As shown in Table 4, phenol and substituted phenols were acetylated in quantitative yield albeit after longer reaction time in comparison with alcohols.

To check the recyclability and reusability of the catalyst we studied the acetylation of aniline with acetic anhydride under similar



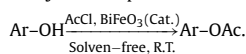
Scheme 3. The proposed catalytic cycle for the acetylation reaction on the surface of BiFeO₃ nanopowder.

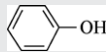
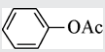
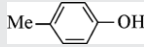
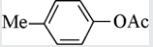
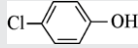
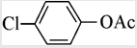
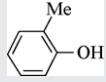
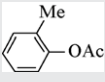

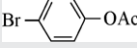
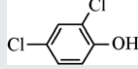
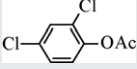
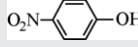

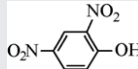
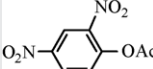


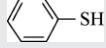
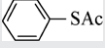
Table 3Acetylation of alcohols with acetyl chloride over BiFeO nanopowder as a heterogeneous catalyst^a.

Entry	Alcohol	Product	Time (min)	Yield ^b (%)
1			12	92
2			10	95
3			10	93
4			10	96
5			12	93
6			15	95
7			15	94
8			20	75
9			20	90
10			25	88
11			20	90
12			25	86
13			25	85
14			28	78
15			20	92
16			45	60
17			30	90
18			30	85
19			30	86
20			30	88

^a Reaction conditions: alcohol (1 mmol), acetyl chloride (1 mmol), catalyst (100 mg), without solvent at rt.^b Yields are for isolated pure products.

Table 4
Acetylation of phenols with acetyl chloride over BiFeO₃ nanopowder as a heterogeneous catalyst^a.



Entry	Phenol	Product	Time (min)	Yield ^b (%)
1			24	88
2			20	95
3			24	95
4			25	94
5			25	93
6			28	92
7			35	89
8			40	85
9			28	92
10			25	86

^a Reaction conditions: phenol (1 mmol), acetyl chloride (1 mmol), catalyst (100 mg), without solvent at rt.

^b Yields are for isolated pure products.

reaction conditions. After completion of the reaction the catalyst could be separated by filtration and reused as such for subsequent experiments (five times). The yields of the product were consistent, indicating the reusability of the catalyst without loss of activity (Table 5). Indeed, the XRD of the spent catalyst revealed no structural changes. For instance, the XRD of the recovered catalyst after 5th run is shown in Fig. 4 which is the same as the XRD of fresh catalyst in Fig. 1.

On the basis of previously reported mechanisms [23] and our observations in the course of this reaction, the mechanism shown in Scheme 3 is proposed. According to this mechanism, the carbonyl group of acetic anhydride or acetyl chloride is activated by coordination to BiFeO₃ nanopowder. Then, the activated carbonyl reacts with substrates to give the corresponding acetates.

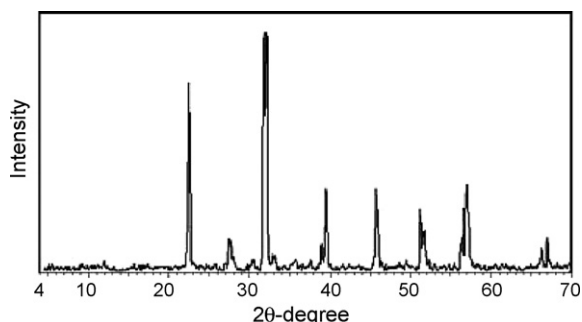


Fig. 4. XRD pattern of recovered BiFeO₃ catalyst after fifth run.

Table 5
Reuse of the catalyst for acetylation of aniline (Scheme 1)^a.

Cycle	0	First	Second	Third	Fourth	Fifth
Yield of 2 ^b (%)	98	96	96	95	94	95

^a Reaction conditions: aniline (1 mmol), acetic anhydride (1 mmol), catalyst (100 mg), without solvent at rt, time: 5 min.

^b Yields are for isolated pure acetanilide.

In any metal oxide catalyst, chemical reactions take place mainly on the surface of the particles and surface atoms make a distinct contribution to its catalytic activity [23c]. In fact, the atoms exist on the particle surfaces behave as the Lewis acid centers where the chemical reaction could be catalytically activated. Moreover, the nanopowder particles have more surface atoms as compared with bulk powder. Therefore, the high catalytic activity of BiFeO₃ nanopowder can be attributed to more surface atoms, participating at the reaction.

4. Conclusions

In general, we have developed an efficient catalytic procedure for acetylation of various amines, alcohols and phenols by use of nano-size BiFeO₃ as recyclable heterogeneous catalyst under solvent-free mild reaction conditions. Among the various substrates studied, acetylation of anilines and primary aliphatic amines proceeded rapidly. The BiFeO₃ catalyst was easily prepared and reusable without loss of activity. To our knowledge, this is the first report of catalytic acetylation on a perovskite-type mixed oxide.

Acknowledgement

The financial support from the Lorestan University Research Council for this work is greatly acknowledged.

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