

Study of acetylation of benzylic alcohols over BiFeO_3 , $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$, and $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ nano powders

Seyed Ali Hosseini^{a,*}, Elham Paknahad^b, Abdolali Alemi^c, Akbar Arkak^a

^aDepartment of Applied Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran.

^bDepartment of Chemistry, University of Saskatchewan, Saskatoon, Canada.

^cDepartment of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran.

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ABSTRACT

BiFeO_3 (BFO), $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$ (BSEFO), and $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ (BSCFO) nano powders were prepared by the sol-gel combustion method and the catalytic performances were evaluated in the acetylation reaction of benzyl alcohol. The physical chemical properties of the catalysts were characterized by using XRD, FT-IR, scanning electron microscope (SEM), EDX and BET surface. The efficient acetylation of benzyl alcohol was carried out over all the nano powders using acetyl chloride/ acetonitrile at room temperature. Among the nano powders, BSCFO showed the highest catalytic performance and the yield of benzyl acetate was 89, 45, and 69 percent over BSCFO, BFO, and BSEFO, respectively. Partial substitution of Sm-Eu and Sm-Cd in bismuth ferrite improved the catalytic performance and increased the specific surface area of the catalysts. A direct relationship resulted between the catalytic performance and the specific surface of catalysts, where BSCFO with the highest surface area ($11.7\text{m}^2/\text{g}$) exhibited the superior catalytic performance. The quantitative yield for the acetate product also resulted for the acetylation of p-methyl benzyl alcohol, p-nitro benzyl alcohol and p-chloro benzyl alcohol on BSCFO. The catalysts showed good reusability in the process. The study confirmed that the catalysts could be promising for the acetylation of alcohols.

Keywords: Europium, Samarium, Ferrite oxide, Nano perovskite, Acetylation.

1. Introduction

Perovskite-type mixed oxides (ABO_3) are one of the most important inorganic solids which have been extensively used as catalysts for many industrial reactions, including hydrocarbon oxidation [1-4], NO_x decomposition [5], oxidation of CO [6] and NH_3 . [7] Perovskite mixed oxides are characterized by a 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 [8]. The acetylation of alcohols is one of the most useful transformations in organic synthesis [10-12]. However, in this process to overcome some problems such as use of excess acetylating agent, use of expensive and moisture sensitive catalysts, tedious preparation of catalysts, harsh reaction conditions, utilization of halogenated

volatile organic solvents and poor yields of the desired products and owing to the growing environmental considerations, development of green processes using heterogeneous catalysts has aroused great interest in recent years [13]. Heterogeneous catalysts are more advantageous over homogeneous catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be reused several times, making the process more economical and environmentally viable [14]. BiFeO_3 or BFO is one of the representative multi ferric materials and has attracted much attention in recent years [15]. The sol-gel process is also widely used for preparing pure-phase powders and thin films. In the sol-gel synthesis of BFO, the sol is usually prepared based on the citric acid route [16-18]. Doping BFO with a foreign atom at either A or B site of the ABO_3 lattice has been shown to play an important role in altering its properties [19]. For example, substitution of Bi^{3+} with rare-earth (RE) elements, such as La^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} resulted in a

*Corresponding author email: a.hosseini@urmia.ac.ir
Tel.: +98 44 3275 2026

remarkable improvement of the ferroelectric and ferromagnetic properties of BFO, which could possibly lead to enhanced Magneto-electric effect [20]. Recently, it has been reported that bismuth ferrite was used for the catalytic acetylation of functional groups [9]. However, there is no report in the literature on the study of (samarium-europium) and (samarium-cadmium) simultaneously replaced BiFeO_3 as a heterogeneous catalyst.

The objectives of these works were to synthesize the BiFeO_3 , $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$, and $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ by sol gel combustion method and to study the role of cadmium and europium in improvement of activity of modified catalysts in acetylation reaction of benzylic alcohols.

2. Experimental

2.1. Catalyst preparation

BiFeO_3 was prepared by a sol-gel process using bismuth nitrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$] and iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] as starting materials [2, 21, 22]. First, stoichiometric amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in a minimum amount of distilled water were mixed. The citric acid was then added into the nitrate solution such that the molar amount of citric acid was equal to the total molar amount of nitrates in the solution. The resultant solution was transparent, brownish, and clear. The mixture was stirred for 3 hours at 80°C to obtain the gel. Then, the powder was annealed at 600°C for 6 h in the furnace to obtain single-phase BiFeO_3 crystalline material.

The samples with the composition $\text{Bi}_{1-x}\text{Sm}_{x/2}\text{Eu}_{x/2}\text{FeO}_3$ ($x=0.14$) and $\text{Bi}_{1-x}\text{Sm}_{x/2}\text{Cd}_{x/2}\text{FeO}_3$ ($x=0.14$) were prepared by a sol-gel method. The analytical grade $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sm_2O_3 and Eu_2O_3 and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were used as starting materials. First, we dissolved the equimolar amounts of metal oxides in nitric acid. The citric acid and distilled water were added into the nitrate solution such that the molar amount of citric acid was equal to the total molar amount of nitrates in the solution. The solution was then gently evaporated at 80°C for 3h to obtain a homogeneous mixture and dried into a gel. The dried powder was then calcined at 600°C for 6 hours in order to get single-phase crystalline materials.

2.2. Characterization and measurements

The structure of the nano powders was characterized by powder X-ray diffraction (XRD) with a Bruker X-ray diffractometer using $\text{Cu K}\alpha$ radiation with a nickel filter. The morphology of the powders was examined using scanning electron microscope (SEM, Hitachi S-4200) fitted with an energy dispersive X-ray analyzer (EDX, Hitachi S-4200). Further, the samples were characterized by using an IR spectrophotometer (Bruker-Germany Model Tensor 27) to understand the

aspect of binding in the samples within a range of $400\text{--}4000\text{ cm}^{-1}$ using KBr powder. The specific surface area was calculated by the BET method using nitrogen.

2.3. General procedure for acetylation of benzylic alcohols

The catalyst (25 mg) was added to the mixture of acetyl chloride (5mmol), benzylic alcohols (5mmol), and acetonitrile solvent (1ml). The reaction mixture was stirred for 1h at room temperature. The progress of the reaction was followed by GC. After the reaction completion, the products were extracted with CH_2Cl_2 and filtered to remove BiFeO_3 . The organic phase was treated with saturated NaHCO_3 solution and dried over anhydrous sodium sulfate. The solvent was removed under vacuum to afford the pure product. The products were characterized by GC-MS.

At the end of benzyl alcohol acetylation, the catalyst was filtered, washed with dichloromethane, dried at 200°C for 2 h, and reused in the reaction for three times.

3. Results and Discussion

Fig. 1 shows the powder XRD patterns of BiFeO_3 and $\text{Bi}_{1-x}\text{Sm}_{x/2}\text{Eu}_{x/2}\text{FeO}_3$ ($x=0.14$) and $\text{Bi}_{1-x}\text{Sm}_{x/2}\text{Cd}_{x/2}\text{FeO}_3$ ($x=0.14$) samples.

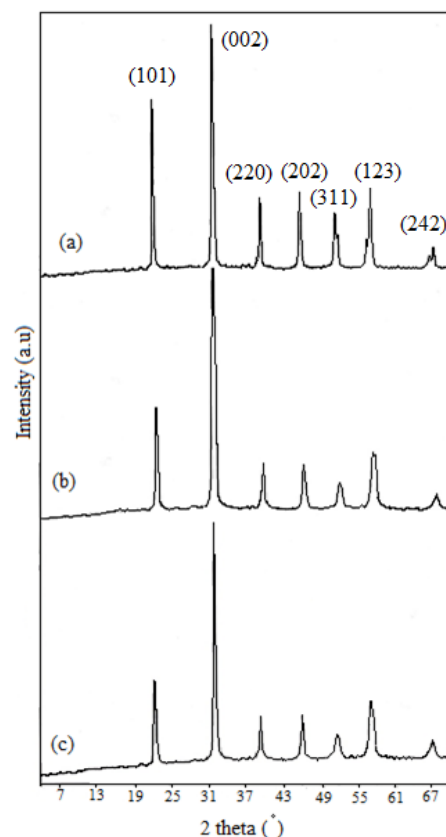


Fig. 1. X-ray diffraction patterns of catalysts. (a) BiFeO_3 , (b) $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$ ($x=0.14$), (c) $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ ($x=0.14$).

This pattern showed only the peaks corresponding to perovskite-type BiFeO_3 (JCPDS File No. 20-169), which crystallizes in the rhombohedral system. No additional peaks secondary impurities such as Fe_2O_3 , Bi_2O_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ were detected [23] in pure and co-doped nanoparticles, indicating the doping of Eu, Sm, and Cd in the structure of BiFeO_3 . The mean crystallite size of perovskites was estimated by Scherrer formula, $D = (0.89 \lambda) / (\beta \cos \theta)$, where λ is the wavelength of $\text{Cu K}\alpha$ radiation, β is the corrected full width at half maximum (FWHM), and θ is the Bragg angle. The crystallite size of BiFeO_3 , $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$, and $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ was 61.3, 53.7, and 47 nm, respectively. It is concluded that partial introducing of Sm, Eu, and Cd decreased the crystallite size.

The smaller crystallite size is due to the smaller size of doped ions as compared to those of Bi^{3+} ions, which results in lattice contractions. In addition, the results of different doping of Eu and Cd (not reported here) demonstrated that the crystallite size decreased with an increase in loading amount.

Further, confirmation about the formation of perovskite structure in the synthesized samples was carried out by FTIR spectroscopy. Fig. 2 shows the FTIR spectra of BFO, BSEFO, and BSCFO. Two fundamental absorptions are observed at about 430 and 554 cm^{-1} . These bands are attributed to O-Fe-O bending and Fe-O stretching vibrations of FeO_6 octahedral unit [24] and also due to the BiO_6 tetrahedral structure unit. [25] No significant shift is observed due to (Sm-Eu) and (Sm-Cd) doping, which can be attributed to the low amount of both (Sm-Eu) and (Sm-Cd) in the doped samples. However, it seems that the distinguished bands in the spectra of the doped catalysts are broader to some extent because of various distributions of cation. These findings prove the formation of the perovskite structure which is in agreement with XRD results. The shape, size and size distribution of the particles were determined by scanning electron microscopy and SEM micrographs are shown in Fig. 3.

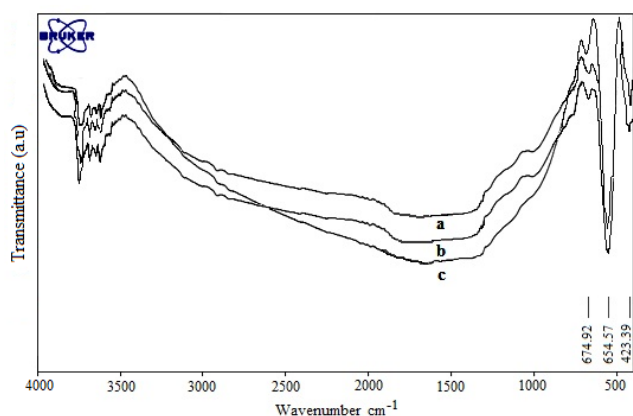


Fig. 2. FT-IR spectra of (a) BiFeO_3 , (b) $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$ ($x=0.14$), (c) $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ ($x=0.14$)

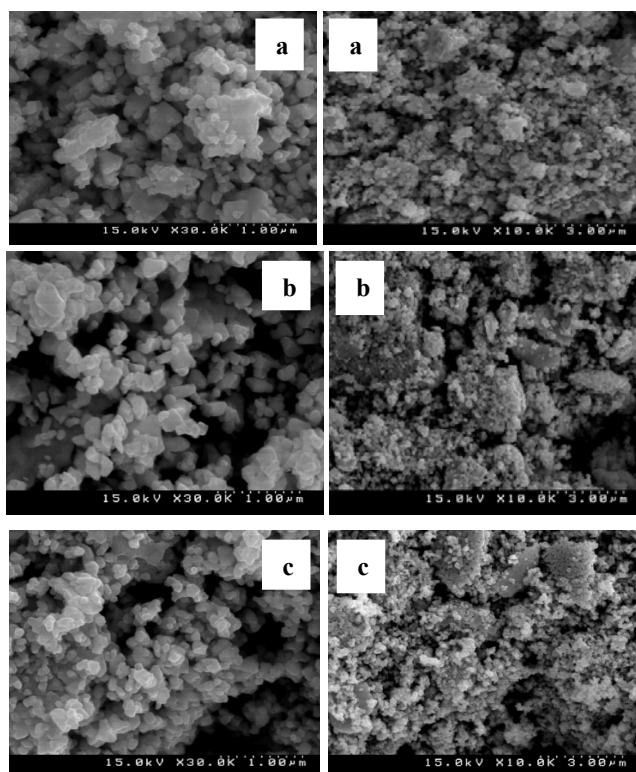


Fig. 3. SEM micrographs of (a) BiFeO_3 , (b) $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$, (c) $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$

It was observed that the particles are agglomerated, and a high interconnection of the grains can be seen from Fig.3. However, particles in all samples are aggregated clusters. Further, reduction of particle size in co-doped BiFeO_3 can be observed.

The chemical compositions of pure and co-doped BiFeO_3 nanoparticles were determined using EDX technique, which are shown in Fig. 4 and the atomic percentages are presented in Table 1. Besides, the obvious signals for O, Bi, and Fe, the EDX spectra show signals of Sm, Eu and Cd in the doped samples. In addition, EDX results confirmed the atomic ratio and the stoichiometry of the compounds.

Fig. 5 shows the N_2 adsorption-desorption isotherms of the catalysts. From the isotherms, the specific surface area of the catalysts was determined by BET method and the results are presented in Table 2. The specific surface areas of BFO, BSEFO, and BSCFO catalysts were 9.6, 10.1, and 11.7 $\text{m}^2 \text{g}^{-1}$, respectively. The higher surface of BSCFO and BSEFO is attributed to distribution of the smaller particle size in the samples as confirmed by SEM. Therefore, there is a good correlation between SEM and BET results.

The catalytic performance of the nano powders was tested in the acetylation of benzylic alcohols, which was the main objective of the work. Once the perovskites were characterized, they were tested in the acetylation of benzylic alcohols.

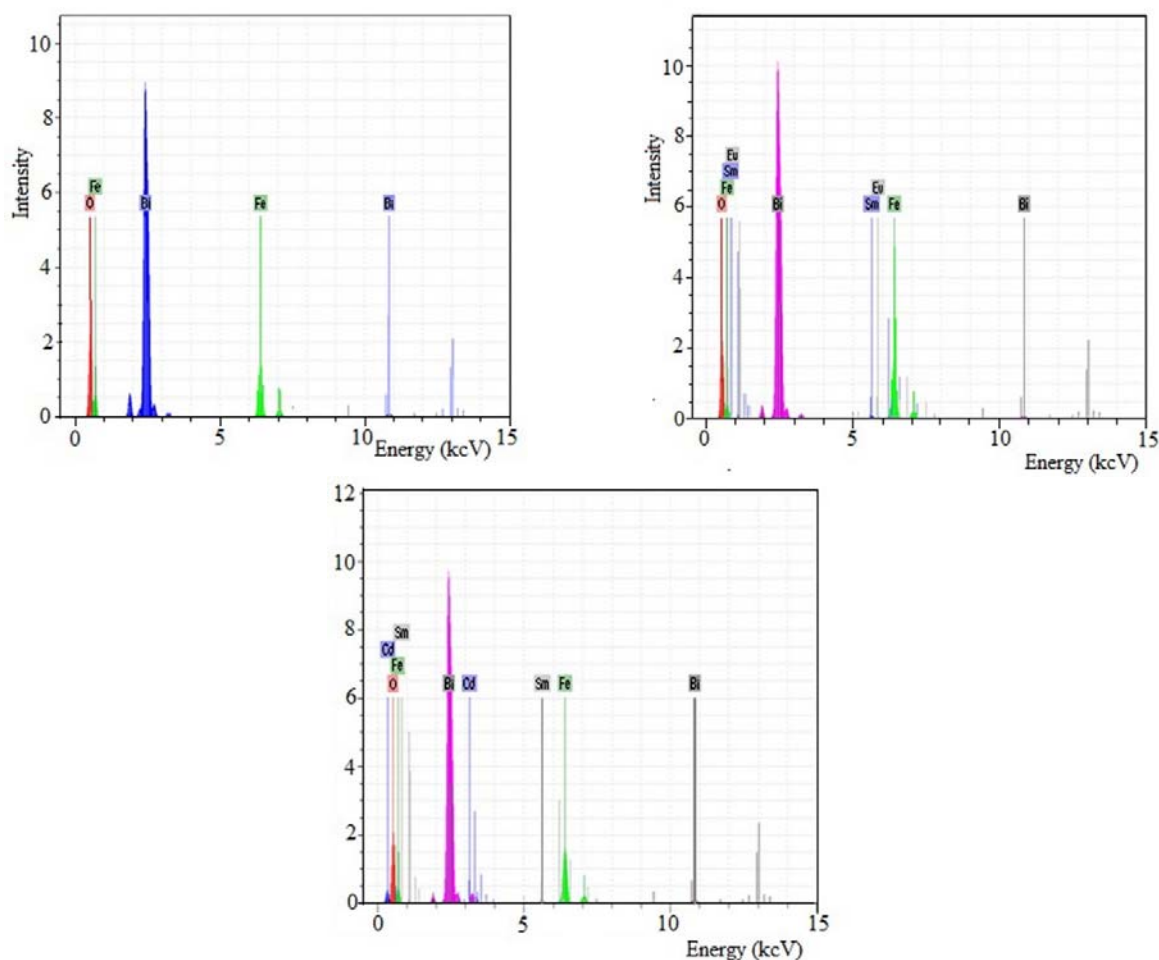


Fig. 4. EDX analysis of a) BiFeO_3 , b) $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$ ($x=0.14$), c) $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ ($x=0.14$).

The main product of the acetylation of benzylic alcohol is benzylic acetate. The acetylating agent of the reaction was acetyl chloride in the acetonitrile solvent.

It is reported in the literature that the catalyst plays the prominent role in the reaction. The acetylation of benzylic alcohols with acetyl chloride did not proceed in the absence of a catalyst. Our results are in agreement with the results reported in Ref. (17) about the blank experiment.

In this study, the yield of the benzyl acetate formation was considered as the criteria of activity and selectivity of the catalysts. The yield of the production of benzyl acetate over the catalysts is presented in Table 3.

The results showed that the yield of benzyl acetate production increased when reactions catalyzed with Sm, Eu and Sm, Cd doped catalysts. The yields of benzyl acetate production over the BFO, BSEFO, and BSCFO were 45, 69, and 89 percent, respectively (Table 3).

It is reported in the literature that the catalytic performance of perovskite oxides depends on their specific surface area [26]. The surface area is an effective factor in the activity of the catalyst, because the reaction takes place on the catalyst surface [27]. A direct relationship was found between the surface area and catalytic performance of the catalysts where BSCFO with the high surface area ($11.7 \text{ m}^2/\text{g}$) showed the highest activity for benzyl acetate production.

Table 1. EDX results for weight percentages of catalysts.

Catalyst	Bi	Sm	Eu	Cd	Fe	O
BiFeO_3	65.10	-	-	-	20.36	14.54
$\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Eu}_{0.07}\text{FeO}_3$	62.26	1.56	1.85		20.86	13.47
$\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$	59.92	3.02		1.44	21.64	13.98

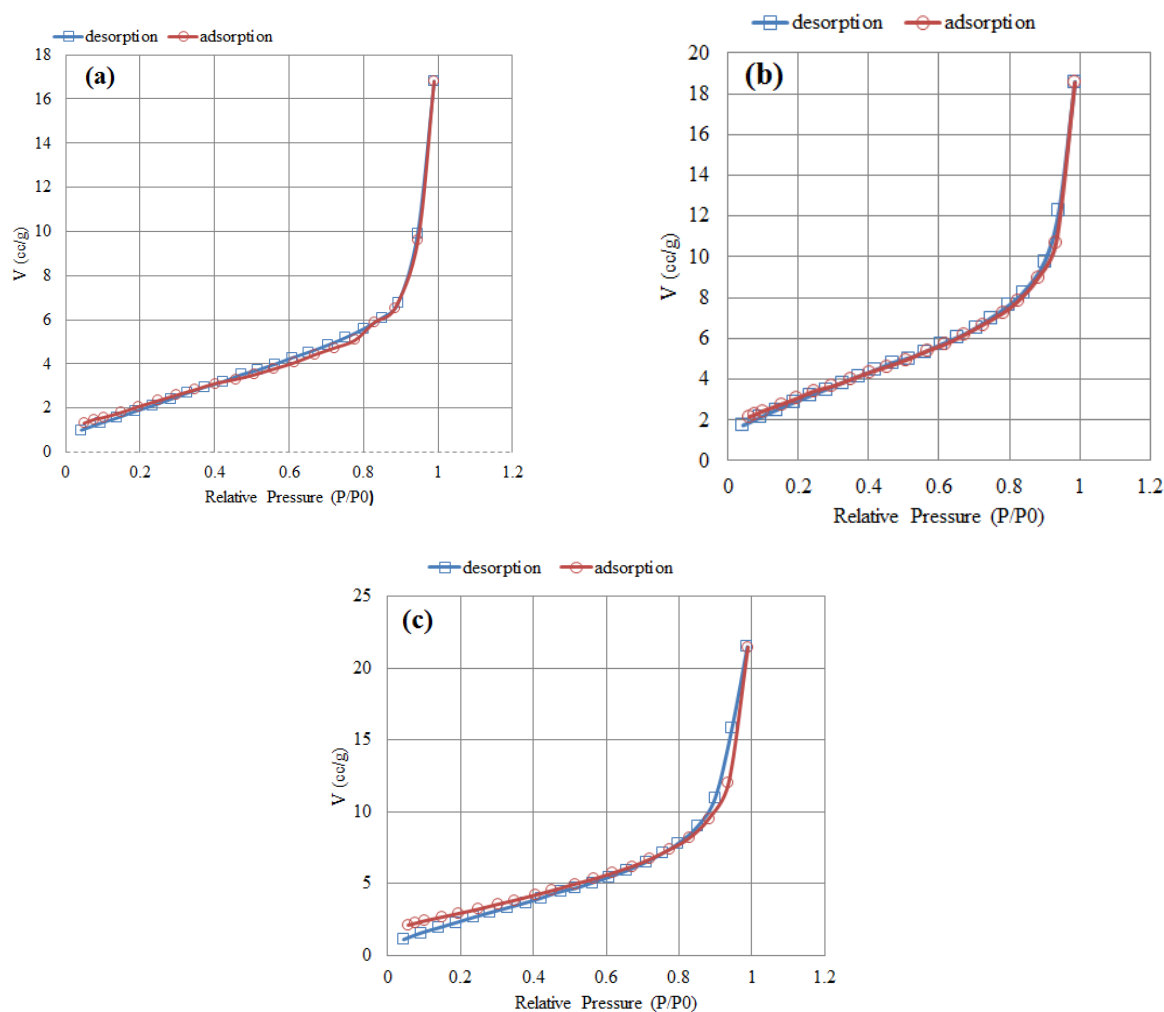


Fig. 5. N₂ adsorption-desorption isotherm of the catalysts: BFO (a), BSEFO (b) and BSCFO (c).

Therefore, the high catalytic activity of Bi_{0.86}Sm_{0.07}Cd_{0.07}FeO₃ (BSCFO) nano powder is attributed to the more specific surface area (participating at the reaction), compared with pure BiFeO₃ as well as the synergistic effect of Sm and Cd with bismuth atoms. The metallic atoms existing on the particle surfaces behave as the Lewis acid centers where the chemical reaction could be catalytically activated. Partial replacement of A with some cations can generate oxygen vacancies and/or change the valence state of original cations and enhances the activity of the catalyst [2, 3, 28].

In the case of the mechanism of the reaction, the following mechanism (Fig. 6) was proposed for acetylation of benzylic alcohols with acetyl chloride based on GC-MS and GC results.

According to this mechanism, the catalyst activates the carbonyl group in acetyl chloride and the activated carbonyl reacts with benzylic alcohols to give benzylic acetates.

Table 2. BET measurement pure and co-doped BiFeO₃ nanoparticles.

Sample	Specific surface area (m ² /g)
BiFeO ₃	9.6
Bi _{0.86} Sm _{0.07} Eu _{0.07} FeO ₃	10.1
Bi _{0.86} Sm _{0.07} Cd _{0.07} FeO ₃	11.7

Table 3. Benzyl acetate production by acetylation of Benzyl alcohol with acetyl chloride over BFO, BSEFO and BSCFO nano powders as heterogeneous catalysts.^a

Catalyst	Yield (%)
BiFeO ₃	45
Bi _{0.86} Sm _{0.07} Eu _{0.07} FeO ₃	69
Bi _{0.86} Sm _{0.07} Cd _{0.07} FeO ₃	89

^aReaction conditions: benzyl alcohol (5 mmol), acetyl chloride (5 mmol), catalyst (25 mg) with acetonitrile solvent (1 ml), room temperature, 1 h

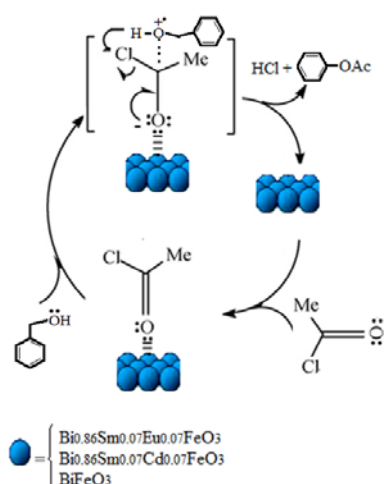


Fig. 6. The proposed catalytic cycle for the acetylation reaction on the surface of BFO, BSEFO, and BSCFO nano powders.

It is believed that the activation of carbonyl is done highly on doped catalysts. Solvolyses of acetyl chloride show a high sensitivity to changes in solvent ionizing power, consistent with C-Cl bond cleavage [29, 30].

Regeneration and reusing of heterogeneous catalyst is an important factor. In order to study the reusability of the catalyst, it was filtered and dried after the reaction was completed. Then, it was calcined at 200°C and resulted in the process under similar conditions for subsequent experiments (three times). The yields of the product were consistent, indicating the reusability of the catalysts without loss of activity.

The structure of the spent catalysts was characterized by XRD. The XRD characterization of the spent catalysts revealed no structural changes. For instance, the XRD patterns of the recovered catalysts after the third run, are shown in Fig., which is similar to the XRD patterns of the fresh catalysts in Fig. 7.

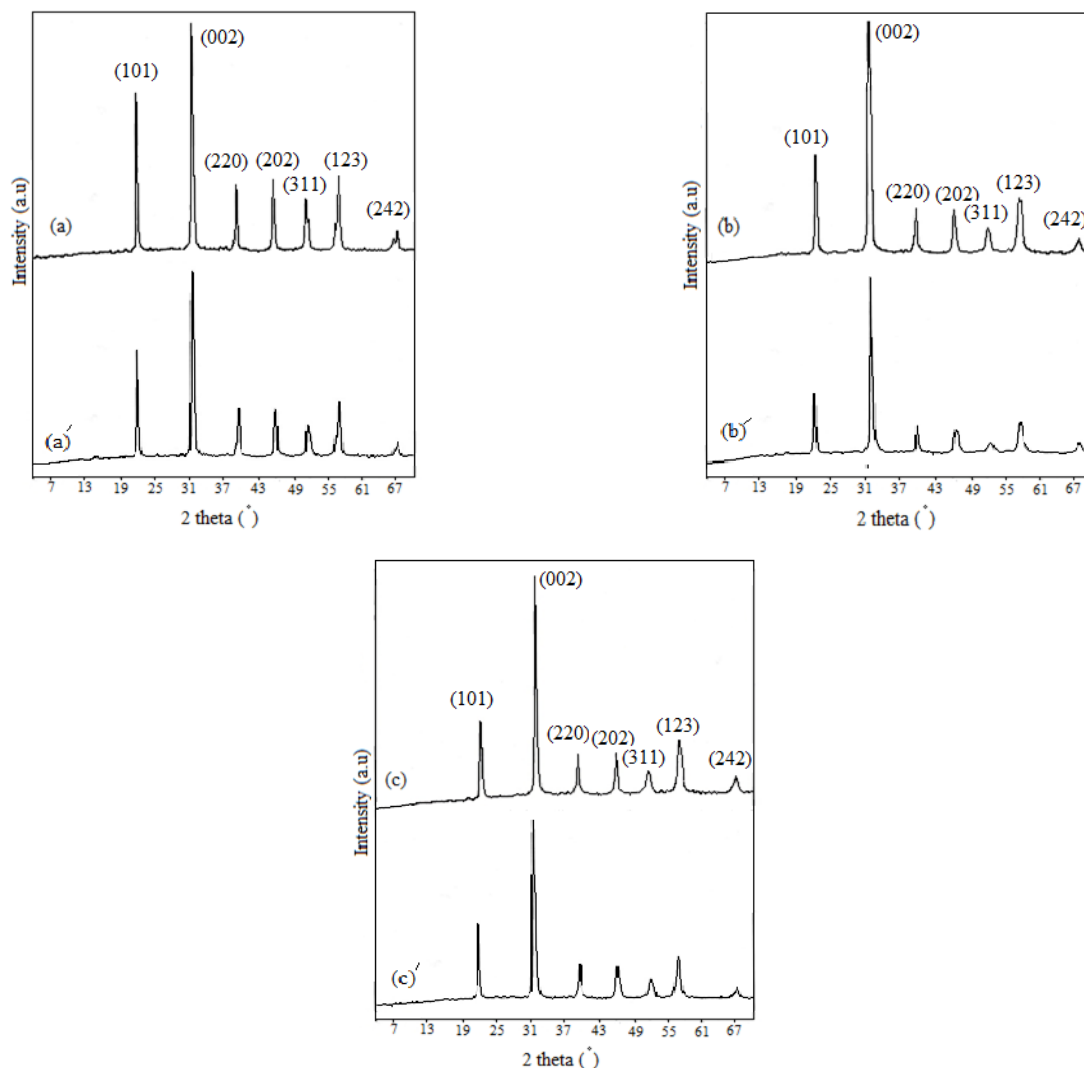


Fig. 7. XRD pattern of recovered BiFeO₃ catalysts after third run (a) BiFeO₃ (x=0), (b) Bi_{0.86}Sm_{0.07}Eu_{0.07}FeO₃ (x=0.14), (c) Bi_{0.86}Sm_{0.07}Cd_{0.07}FeO₃ (x=0.14). a', b' and c' are the used catalyst.

Furthermore, the activity of the most active catalyst under study, i.e. $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ (BSCFO) was tested in acetylation of alcohols containing different electron withdrawing and donation groups by acetyl chloride in acetonitrile. The test conditions were the same with previous tests. The results of the test are presented in Table 4. The tested alcohols were benzylic alcohols i.e. benzyl alcohol, p-methyl benzyl alcohol, p-nitro benzyl alcohol and p-chloro benzyl alcohol, all of which were primary alcohol. The selected product for all alcohols was corresponding acetates in quantitative yields. Methyl is an electron donating group, whereas nitro and chloride groups are an electron withdrawing group. The results confirmed not only electron-rich benzylic substrates, but also electron deficient ones were converted to the acetate derivatives in high yield (Table 4). However, the results showed that methyl as an electron donating group increases the yield of benzyl acetate production. The yield of p-nitro benzyl alcohol and p-chloro benzyl is lower than that of benzyl alcohol.

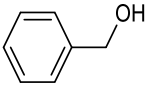
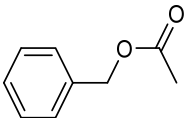
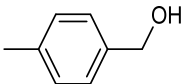
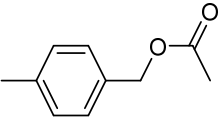
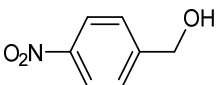
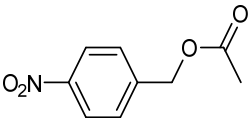
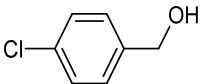
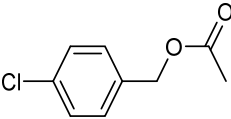
Table 5 presents the comparison of activity of $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ (BSCFO) catalyst with that of some catalysts used for the acetylation of benzyl alcohol reported in the literature [31-35]. The yield of the production of benzyl acetate from benzyl alcohol is shown in the table. Apparently, the value of the yield is similar, but it should be noted that the amount of our catalyst is at least a quarter of that used in the references 31-45. The usual amount of catalyst is 100 and 500 mg for 1mmol of benzyl alcohol, whereas the amount of catalyst in our experiment was 25 mg for 1 mmol.

This means that the activity of our catalysts is much higher than that of a catalyst in the literature. When the procedure was tested with 100 mg of BSCFO, the yield of more than 92% was achieved in less than ten minutes. The comparison indicates that the catalyst is promising for the acetylation process and optimizing the condition could lead to reach more yield of acetate product.

4. Conclusions

In general, we have carried out an efficient catalytic procedure for the acetylation of benzylic alcohols by use of nano-size BiFeO_3 and novel co-doped BiFeO_3 catalysts as a recyclable heterogeneous catalyst under acetonitrile solvent reaction conditions. The pure and co-doped BiFeO_3 catalysts were easily prepared and reusable without loss of activity. To our knowledge, this is the first report of catalytic acetylation on (Samarium-Europium) and (Samarium-cadmium) simultaneously replaced BiFeO_3 as a heterogeneous catalysts and co-doped system improved catalytic properties of BiFeO_3 . The study demonstrated the role of substitution of co-doped (Sm-Eu) and (Sm-Cd) in the improvement of the activity of catalysts. BSCFO, the most active catalyst in test series showed the promising activity in the conversion of substrates with electron withdrawing and donation groups to the corresponding acetates in quantitative yields without any evidence for the formation of side products. It is concluded that these catalysts could be promising catalysts for the acetylation of other alcohols even phenols and amines.

Table 4. Acetylation of benzylic alcohols derivatives with acetyl chloride over $\text{Bi}_{0.86}\text{Sm}_{0.07}\text{Cd}_{0.07}\text{FeO}_3$ nano catalyst.^a

Entry	Alcohol	Product	Yield (%)
1			89
2			92
3			72
4			88

^aReaction conditions: benzyl alcohol derivatives (5 mmol), acetyl chloride (5 mmol), catalyst (25 mg) with acetonitrile solvent (1 ml), room temperature, 1h.

Table 5. The comparison of different catalysts in acetylation of benzyl alcohol to benzyl acetate.

Entry	Catalyst	Condition (Catal amount/temperature/time)	Yield%	Ref.
1	Bi _{0.86} Sm _{0.07} Cd _{0.07} FeO ₃	25 mg/r.t/1h	92	-
2	Bi _{0.86} Sm _{0.07} Cd _{0.07} FeO ₃	100 mg/ r.t /<10 min	93%	-
3	H ₁₄ [NaP ₅ W ₂₉ MoO ₁₁₀]	100 mg/ r.t /15 min	95	[31]
4	H ₆ [P ₂ W ₁₈ O ₆₂]	100 mg/ r.t /40 min	95	[31]
5	Graphite bisulphate	350 mg/r.t./5 min	93	[32]
6	CoCl ₂	260 mg/r.t./1min	75	[33]
7	2% Ni/SiO ₂	500 mg/65 °C/10h	70	[34]
8	5% Ni/SiO ₂	500 mg/65 °C /3h 30min	80	[34]
9	10% Ni/SiO ₂	500 mg/65 °C /3h	97	[34]
10	ZnAl ₂ O ₄ @SiO ₂ nanocomposite	100 mg/65 °C/22 min	92	[35]

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