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Hydrothermal Synthesis of a Solid Acid Catalyst Based on Bromosodalite and Its Application in Esterification

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ARTICLE DETAILS

Article history:

Received 24 February 2026

Accepted 11 March 2026

Available online 15 April 2026

Keywords:

Stearic Acid
L-Ascorbyl-6-Stearate
Solid Acid Catalyst
Heterogeneous
Hydrothermal

ABSTRACT

Coal fly ash, an abundant industrial waste, was valorized for the synthesis of bromosodalite through a hydrothermal process. The synthesized material was subsequently acid-treated to generate catalytically active acidic sites, transforming it into a heterogeneous solid acid catalyst. The structural and morphological properties of the catalyst were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The acid-treated bromosodalite was then evaluated as a heterogeneous catalyst for the esterification of *L*-ascorbic acid with stearic acid to produce ascorbyl stearate, a value-added ester widely used in food, cosmetic, and pharmaceutical applications. The catalytic performance demonstrated successful esterification under heterogeneous conditions, offering a sustainable alternative to conventional homogeneous acid catalysts. The use of fly ash-derived bromosodalite not only reduces environmental waste but also overcomes drawbacks associated with homogeneous catalysis, such as corrosion, difficulty in catalyst recovery, and waste generation. This study highlights the potential of waste-derived solid acid catalysts for green and efficient esterification processes.

1. Introduction

Esterification reactions play a crucial role in the synthesis of fine chemicals, pharmaceuticals, food additives, and cosmetic ingredients. Traditionally, these reactions are catalysed by homogeneous mineral acids such as sulfuric or hydrochloric acid, which, despite their high catalytic efficiency, suffer from several disadvantages including equipment corrosion, difficulty in catalyst separation, generation of acidic waste, and environmental concerns. These limitations have driven increasing interest in the development of heterogeneous solid acid catalysts that offer ease of recovery, reusability, and improved process sustainability [1-5].

Ascorbyl stearate, an ester of *L*-ascorbic acid and stearic acid, is an important lipophilic antioxidant extensively used in food preservation, cosmetics, and pharmaceutical formulations. However, the esterification of *L*-ascorbic acid is challenging due to its thermal sensitivity and multiple hydroxyl groups, which require controlled reaction conditions and effective catalytic systems. Conventional homogeneous acid-catalyzed processes, while effective, are not environmentally benign and pose challenges for downstream purification [6-9]. In recent years, zeolite-based and aluminosilicate materials have gained attention as solid acid catalysts due to their tunable acidity, thermal stability, and structural robustness. Among these materials, sodalite-type frameworks have shown promise in catalytic applications owing to their cage-like structure and ion-exchange capabilities. Bromosodalite, a halide-containing aluminosilicate, can be synthesized via hydrothermal methods and further modified to introduce acidic functionalities suitable for catalysis [10-13]. Coal fly ash, a by-product of coal combustion in thermal power plants, is generated in large quantities worldwide and poses significant disposal and environmental challenges. Rich in silica and alumina, fly ash serves as an inexpensive and sustainable precursor for the synthesis of zeolitic materials. Converting fly ash into value-added catalysts not only mitigates waste disposal issues but also contributes to circular economy and sustainable material development [14-18].

In the present study, bromosodalite (Br-SOD) was synthesized from coal fly ash using a hydrothermal process and subsequently acid-treated to enhance its acidic properties. The resulting material was thoroughly

characterized using FTIR, XRD, and SEM techniques to confirm its structural integrity and surface morphology. The acid-drafted Br-SOD was then applied as a heterogeneous catalyst for the esterification of *L*-ascorbic acid with stearic acid. The successful catalytic performance demonstrates the feasibility of replacing traditional homogeneous acid catalysts with a fly ash-derived heterogeneous system, providing a greener and more sustainable approach for ester synthesis.

2. Experimental Methods

2.1 Materials

Coal fly ash (CFA) as a source of alumina and silica was collected from a thermal power plant in Eklahra, Nashik, Maharashtra, India, being generated by pulverized bituminous coal combustion and analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and results obtained are shown in Table 1. The reagents used to activate the fly ash were sodium hydroxide (NaOH), (99%, Aldrich chemicals), KBr (99%, Aldrich chemicals), and distilled water. *L*-ascorbic acid, Stearic acid, *n*-hexane, and DMF from Sigma Aldrich chemicals. All chemicals are used without further purification.

Table 1 Chemical composition of coal fly ash by ICP-OES analysis

Components	Composition Wt. %
SiO ₂	58.33
Al ₂ O ₃	26.01
Fe ₂ O ₃	4.91
TiO ₂	1.27
CaO	1.05
MgO	0.72
K ₂ O	1.03
Other	6.68

2.2 Bromosodalite (Br-SOD) Synthesis

Adsorbent, Br-SOD Na₈[AlSiO₄]₆(Br₂) has been synthesized from waste coal fly ash (CFA) collected from a thermal power plant located at Eklahra, Nashik, Maharashtra, India. Collected CFA was washed thoroughly by distilled water to remove water soluble content, during washing magnetic material was separated by a magnetic stirrer and magnet. CFA was filtered

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and dried in the oven. Clean and dried CFA was fused with NaOH with equal quantity by mass in a silica crucible at 550 °C for 2 hours in a muffle furnace. The NaOH fused CFA was then mixed with distilled water by a proportion of 1 g/10 mL water and, 7 g of sodium bromide was added to the mixture. The obtained mixture was transformed into a steel-lined Teflon autoclave and kept it for 6 days in the oven at 120 °C. The polycrystalline product was recovered by filtration and washed with deionized water. The recovered product was then dried at 100 °C for 24 h in the oven. Fig. 1 shows flow chart for synthesis of Br-SOD by using coal fly ash.

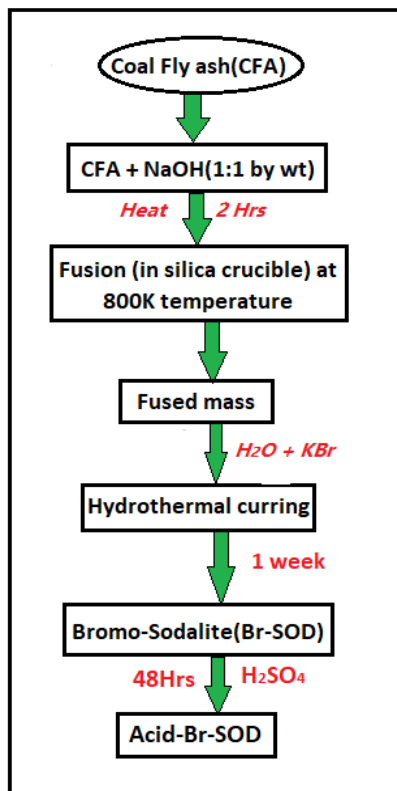


Fig. 1 Flow chart for synthesis of Acid-Br-SOD

2.3 Drafting of Sulfuric Acid onto Br-SOD

The synthesized Br-SOD was further subjected to an acid treatment process to graft sulfuric acid (H_2SO_4) onto its surface. 1 M H_2SO_4 solution was prepared, and the Br-SOD crystals were immersed in the acid solution under continuous stirring at room temperature for 48 hours. This treatment allowed the acid to interact with the sodalite framework, incorporating acidic sites into the structure. After completing the acid drafting, the bromosodalite was filtered and washed several times with deionized water to remove any unreacted sulfuric acid. The washed crystals were then dried at 100 °C for 12 hours to remove residual moisture. The acid-drafted bromosodalite was then subjected to thermal treatment in a muffle furnace to enhance its catalytic properties. The dried material was placed in a silica crucible and heated at 400 °C for 4 hours under a controlled atmosphere. This step ensured the complete incorporation of acid sites into the sodalite structure and enhanced its thermal stability. The gradual heating process also helped in preventing any structural damage to the sodalite framework.

2.4 Binding with Sodium Silicate: Preparation of Binder

To facilitate the more convenient use of the acid-drafted Br-SOD as a heterogeneous catalyst, the material was bound into more convenient forms using an inorganic binder, sodium silicate extra pure (purchased from Sigma Aldrich) of density 1.396 g/mL [19].

2.5 Formation of Catalyst Pellets

The acid-drafted Br-SOD was mixed with the sodium silicate solution (by 7:3 ratio by wt.) to form a paste. This paste was then molded into a small pellet with very mild pressure and was suitable for use and easy to isolate. The molded forms were allowed to dry at room temperature for 24 hours to ensure proper binding and then cured from 30 °C to 300 °C (at 25 °C min^{-1}) and it was then held at this temperature for 3 hrs in a muffle furnace. This curing process solidified the structure, providing mechanical strength and durability during catalytic reactions.

<https://doi.org/10.30799/jacs.S305.26120405>

2.6 Acidic Nature of Acid Br-SOD Catalyst

pH metric titration method was successfully applied to investigate the acidic nature of Br-SOD synthesized. Two types of titrations, blank titration, and back titration, were conducted to qualify the acidic nature of catalyst. The experiment demonstrates the ability of the catalyst to neutralize NaOH, providing insight into its potential applications. In catalytic processes, characterizing acidic catalysts is crucial for their application as acid catalysts [20].

Synthesized acid-Br-SOD catalyst, is hypothesized to exhibit significant acidic properties. This study employs instrumental titration methods to evaluate the ability of catalyst to neutralize the base (NaOH), confirming its acidic nature. Fig. 2 depicts the plot for blank and back titration for pH change with HCl. To measure the neutralization effect of the acid Br-SOD catalyst on NaOH, 100 mL of 0.05 N NaOH was kept in contact with the 25 g solid acid Br-SOD catalyst for 30 minutes. The solution was filtered to remove the catalyst. The filtered 25 mL, NaOH solution was titrated pH-metrically with 0.05 N HCl, and again changes in pH values were recorded, sudden change in pH value indicates neutralization.

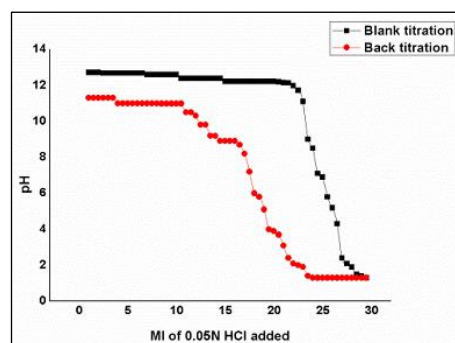
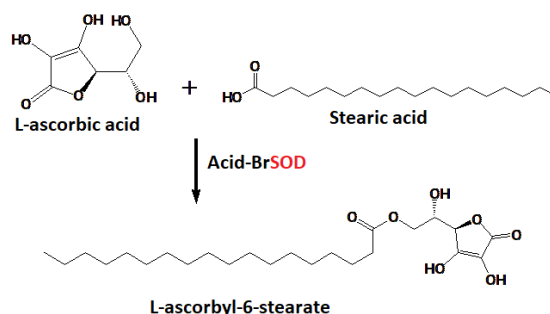


Fig. 2 Investigation of the acidic nature of acid-Br-SOD

The results from the blank titration curve established the baseline NaOH neutralization capacity. In contrast, the back titration graph consistently showed lower volumes of HCl required for neutralization. The reduction in HCl volume in the back titration indicates that the acid Br-SOD neutralized a portion of NaOH. The difference between the average titration volumes from the blank and back titrations qualifies the acidic property of the catalyst. It confirms the presence of acidic sites on the synthesized acid Br-SOD catalyst. This finding supports the potential use of acid Br-SOD in catalysis, particularly in processes requiring acidic conditions.

2.7 Synthesis of L-Ascorbyl Stearate using Br-SOD Acid Catalyst

L-ascorbic and stearic acid were procured from Sigma-Aldrich and utilized without additional purification. Stearic acid was employed as the limiting reagent. The heterogeneous acid-Br-SOD catalyst pellets were placed in a round-bottom flask (reactor) attached to the condenser, followed by the addition of solid stearic acid and L-ascorbic acid, without solvent. The reactor was then placed in a water bath and occasionally agitated until the reaction mixture melted. After 30 minutes, continuous boiling of the reaction mixture was observed, and the acid value was periodically measured and recorded. Once the stearic acid had fully reacted, the reaction mixture was transferred into a beaker containing deionized (DI) water. The solid acid-Br-SOD catalyst remained at the bottom of the round-bottom flask, while a yellowish-white waxy substance floated on the water surface. Unreacted L-ascorbic acid was removed by washing with deionized water. The resulting product was subsequently recrystallized from n-hexane. The scheme 1 for synthesis of L-Ascorbyl stearate is shown below. The final product's identity was confirmed through ^{13}C -NMR and 1H -NMR spectroscopy.



Scheme 1 Synthesis of L-Ascorbyl stearate

degree of aggregation or clustering may be observed in the SEM images. This could enhance catalytic activity by increasing particle-to-particle contact, creating additional pathways for chemical reactions. Acid-Br-SOD is designed with a nanoporous structure, SEM might reveal pores or channels that further enhance the surface area. These pores, if present, would facilitate the diffusion of reactants and improve catalytic efficiency. An SEM study of Acid-Br-SOD with these particle sizes would help characterize its structure and distribution, providing insight into its suitability and efficiency as a catalyst for targeted reactions.

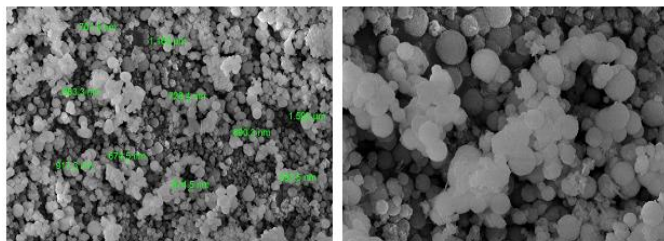


Fig. 7 SEM images of Acid-Br-SOD

3.2.3 XRD Analysis

Fig. 8 presents the X-ray diffraction (XRD) patterns of bromo-sodalite (Br-SOD) and acid-treated bromo-sodalite (Acid-Br-SOD). The diffraction peaks observed in both patterns confirm the crystalline nature of the samples. The prominent reflections appearing at specific 2θ positions correspond to the characteristic (hkl) planes of the sodalite framework. The major intense peak observed around $2\theta \approx 24\text{--}25^\circ$ along with other weaker reflections at higher angles indicates the formation of a well-defined sodalite structure.

In the case of Br-SOD (pattern a), sharp and well-resolved peaks suggest good crystallinity of the material. After acid treatment (pattern b), the overall diffraction pattern remains similar, indicating that the fundamental sodalite framework is preserved. However, slight variations in peak intensity and minor broadening of some reflections are observed, which may be attributed to partial dealumination, removal of extra-framework species, or slight structural modification caused by acid treatment. These changes usually indicate surface cleaning and minor lattice distortion without collapse of the framework. The (hkl) indices corresponding to the respective 2θ values match well with the standard diffraction data reported for sodalite-type materials. The obtained XRD patterns closely resemble the standard pattern listed under JCPDS card number 00-037-0196, confirming the successful formation of the sodalite phase in both samples. The absence of additional impurity peaks further suggests phase purity of the synthesized materials. Therefore, the XRD analysis demonstrates that acid treatment modifies the surface characteristics while retaining the crystalline sodalite structure.

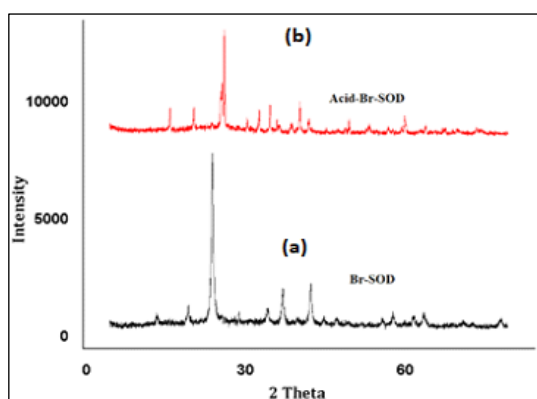


Fig. 8 X-Ray Diffraction pattern of Br-SOD and Acid-Br-SOD

4. Conclusion

The synthesized acid-Br-SOD proved to be an effective solid acid catalyst for the esterification of L-ascorbyl stearate. Characterization confirmed that Br-SOD provides a high surface area because of fine particle size and, upon acid modification, exhibits strong Bronsted acidity, enabling efficient catalytic performance. The catalyst not only promoted successful esterification but also offered the advantages of heterogeneous catalysis, such as ease of recovery and potential reusability. This highlights acid-Br-SOD as a promising candidate for green and sustainable esterification processes, particularly in the synthesis of bioactive esters like L-ascorbyl stearate.

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