



VISTA INTERNATIONAL JOURNAL ON ENERGY, ENVIRONMENT & ENGINEERING



Synthesis of Ethyl Lactate Over Silver Supported on Bentonite Clay Heterogeneous Catalyst.

Poonam Gaikwad*, Ruchita Tidke and V.A. Gite

Department of Chemical Engineering, Jawaharlal Nehru Engineering College, MGM University, Chhatrapati Sambhajinagar, Maharashtra (M.S.), India

*Corresponding Author's E-mail: apoonamg35@gmail.com Mob.: +91-9284466732

A B S T R A C T

Green chemistry is the new emerging trend in chemical and allied industries. It involves designing of process that minimizes or eliminates the use and generation of waste and toxic substances. Though it is not a new term but its development has been accelerated in recent years. Green Catalyst is an important key in Green Chemistry, which is widely used to speed up the reaction speed by lowering the activation energy originally needed for the reaction to take place. Silver Sulphate is supported on Bentonite clay using the wet impregnation method. Bentonite is a natural clay and is widely used in cosmetics, pharmaceuticals, and flavor. industries. Its physicochemical properties, like large surface area, swelling capacity, adsorption characteristics, and cation exchange capacity, make it a significant choice for supporting material. Purified and properly surface-modified bentonite clay is then effectively used in various catalytic reactions involving esterification, oxidation, and condensation reactions. Silver Sulphate is known for its excellent surface characteristics and high catalytic activity. Silver Sulphate ion can be supported on silica gel, alumina, bentonite etc. The supported Ag ions were identified and analyzed using the FTIR test, which measures the infrared absorption of supported Ag ions. The test showed a peak point at 1005.5 cm⁻¹, which concluded that silver sulphate is successfully supported on bentonite. The catalyst was used for the synthesis of ethyl lactate through an esterification reaction using lactic acid and ethanol. Ethyl Lactate is a green solvent that is replacing toluene, xylene, and acetone.



This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords : *Green Chemistry; Silver Sulphate; Bentonite Clay; Esterification; Ethyl Lactate; FTIR Analysis.*

1. Introduction :

Ethyl lactate ($C_5H_{10}O_3$) is an ester which is biodegradable which is widely used as a green solvent because of its top-notch solvency, low toxicity level, and environmental capability. The manufacturing process of ethyl lactate involves an esterification reaction between lactic acid and ethanol, a reaction that is both energy efficient in accordance with the 12 Principles of Green Chemistry. Its applications involve use as a solvent and carrier liquid in pharmaceuticals, flavoring, and preservatives in the food industry, agriculture, cleaning and stripping agent in polymer processing. Its biodegradability, along with non-volatile status, has resulted in making it an excellent choice over petroleum-based solvents.

Conventionally, the synthesis process of ethyl lactate was accelerated with the help of mineral acids such as sulfuric acid and hydrochloric acid. The use of these homogeneous catalysts resulted in high activity presented several challenges. The major challenges include reactor corrosion, separation difficulty from the product, limited recyclability, and effluent neutralization. These drawbacks led to an increase in operational costs and environmental burden and a decrease in sustainability. Thus, researchers have increased focus on the development of efficient heterogeneous catalysts to overcome limitations.

Heterogeneous catalysts offer several benefits over homogeneous ones. These include easy separation of solid catalyst particles from the product via simple filtration or centrifuging to increase recovery and reuse. They reduce corrosion issues, downstream neutralization that enables greener processes. Furthermore, these catalysts have high selectivity due to their excellent surface properties, pore structure, and active sites. Active catalytic species are supported on supports like silica, zeolites, alumina, and clays for stability and increased surface area for reactant accessibility.

Among all the naturally occurring materials, bentonite clay is the most promising support due to its abundance, low cost, layered structure, high surface area, and ion exchange capacity. Bentonite is rich in montmorillonite, which means that there are large interspaces available for the incorporation of reactants and ions. Further, its thermal stability makes it more selective for esterification reactions.

Silver compounds, especially silver sulphate (Ag_2SO_4), have gained spotlight as active catalytic components. They are known for their redox properties, antimicrobial activity, and catalyzing esterification reactions. Supporting silver sulphate on porous bentonite clay combines the oxidative properties of silver sulphate with the high surface area of bentonite clay. The hybrid catalyst not only increased the catalyst activity but also improved stability and reusability.

In this study, silver sulphate was supported on bentonite clay, which was further examined as a heterogeneous catalyst for the synthesis of ethyl lactate. The synthesized catalyst was characterized by spectroscopic techniques like FTIR to confirm the support of silver species on bentonite clay surface. The progress of the esterification reaction was monitored by the titration method. The main objective of the study was to examine the potential of silver sulphate supported on bentonite as an eco-friendly, cheap, and reusable heterogeneous catalyst for green synthesis of ethyl lactate solvent.

2. Materials and Methods :

The chemicals used for the synthesis and method used are discussed as follows.

2.1 Materials :

The chemicals used for the synthesis of the catalyst and ethyl lactate were of analytical grade and were used without further purification. Lactic acid (85% aqueous solution) and ethanol (99.5%) were purchased from standard laboratory suppliers and were employed as reactants for esterification. Silver sulphate with a purity of more than 99% was obtained from the same supplier and used for catalyst preparation. Bentonite clay

was locally sourced from a construction site, which was purified by repeated washing with distilled water and oven-dried. Distilled water was employed throughout the experiment for washing and solution preparation.

2.2 Catalyst Synthesis :

Synthesis of silver sulphate supported on bentonite was carried out in 3 main stages:

- 1) **Pre-treatment of Bentonite Clay :** Raw bentonite clay was dispersed in 1M nitric acid (HNO_3) solution and stirred using a magnetic stirrer for 12 hours at ambient temperature. Acid treatment aimed at increasing the available surface area and active sites for the settlement of silver compounds and separation of insoluble impurities. The treatment clay was thoroughly washed with hot distilled water for complete removal of acid till it reached neutral pH. Clay was then oven-dried at 110°C for 4 hours.
- 2) **Supporting Silver Sulphate :** Hot distilled water was used as a solvent for supporting. A known quantity of Ag_2SO_4 was dissolved in a known amount of water to form an aqueous solution. The solution was then slowly added to the acid-treated bentonite clay with continuous stirring. The mixture was stirred for several minutes to ensure uniform dissociation of silver sulphate ions. The mixture was oven-dried and further processed.
- 3) **Post-Synthesis Treatment :** The impregnated clay was calcined in a furnace at 400°C for 3 hours. Calcination helps in stabilizing silver sulphate species on the clay surface and enhances surface integrity. Finally, the catalyst was crushed to a fine powder and stored in an airtight container for testing.

2.3 Experimental Procedure :

The catalytic performance was analyzed using the Esterification reaction between ethanol and lactic acid to produce ethyl lactate. The experiment was performed in a batch reactor under reflux conditions.

The Esterification reaction was carried out in a 250 mL glass beaker equipped with a reflux condenser, thermometer, magnetic stirrer, and heater. A mixture of lactic acid (0.4M) and ethanol (0.4M) was introduced and mixed with silver sulphate-bentonite catalyst (corresponding to 5wt% of lactic acid). The mixture in the reactor was heated using a heater, and the reaction temperature was maintained at 80°C . The mixture was stirred continuously using a magnetic stirrer under reflux conditions. The samples were withdrawn at regular intervals of 30 minutes.

2.4 Analysis Method :

The unreacted concentration of lactic acid in the reaction mixture at different intervals of time was determined by titration. For each analysis, the sample was filtered and cooled, and then titrated against a standardized solution of 0.2 M using phenolphthalein as an indicator. The titrant volume corresponded to the number of unreacted moles of lactic acid in the mixture.

The lactic acid concentration was calculated using:

$$C_{\text{LA},t} = V_{\text{NaOH}} \times N_{\text{NaOH}} / V_{\text{sample}}$$

where V_{NaOH} = Titrant volume (L), N_{NaOH} = Normality of NaOH ($\text{mol} \cdot \text{L}^{-1}$),
and V_{sample} = Aliquot volume (L).

The percentage conversion of lactic acid was calculated by:

$$X_{\text{LA}} = (C_{\text{LA},0} - C_{\text{LA},t}) / C_{\text{LA},0}$$

where $C_{\text{LA},0}$ = initial concentration of lactic acid (0.4 M).

2.5 Characterization of Catalyst :

The characterization of the catalyst was performed using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra confirmed incorporation of Ag_2SO_4 into bentonite by shifts in Si-O and Al-OH bands.

3. Results and Discussion :

The results are discussed below regarding the characterization and titration analyses.

3.1 Results from the Characterization of catalyst :

The FTIR spectra of bentonite before (Fig. 1) and after silver sulphate loading (Fig.2) were recorded in the range of $400\text{-}4000\text{ cm}^{-1}$. New absorption bands were seen to be appeared in the range of $1100\text{-}1150\text{ cm}^{-1}$, which were due to S-O stretching vibrations from the sulphate group of silver sulphate.

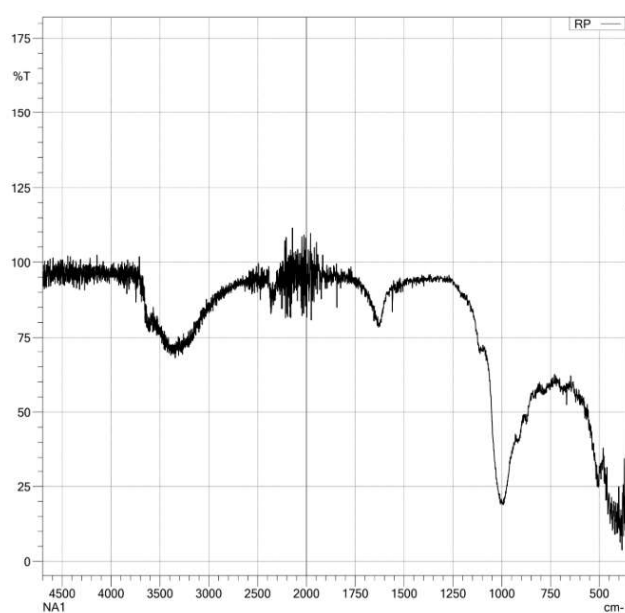


Fig. 1. The FTIR spectra of bentonite before silver sulphate loading

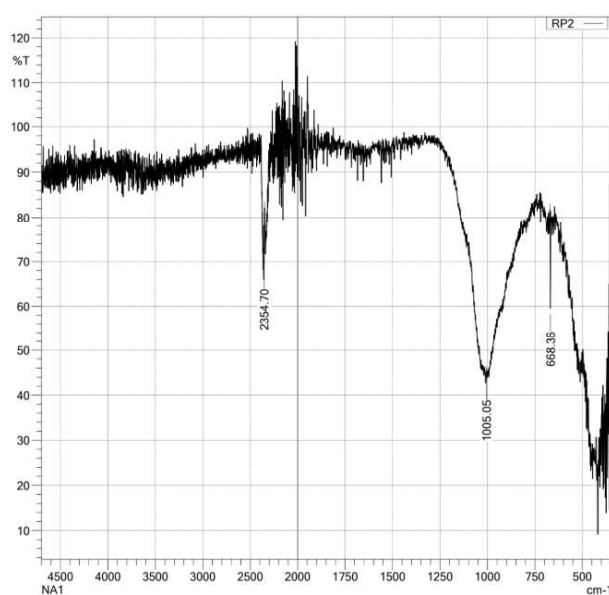


Fig. 2. The FTIR spectra of bentonite after silver sulphate loading

3.2 Titration analysis and discussion :

The results of titration analysis processes are shown in the graphs (Figs. 3a,b). The change in the Lactic acid concentration with time is as shown in Fig. 3(a) while the Esterification conversion with time is as shown in Fig. 3(b).

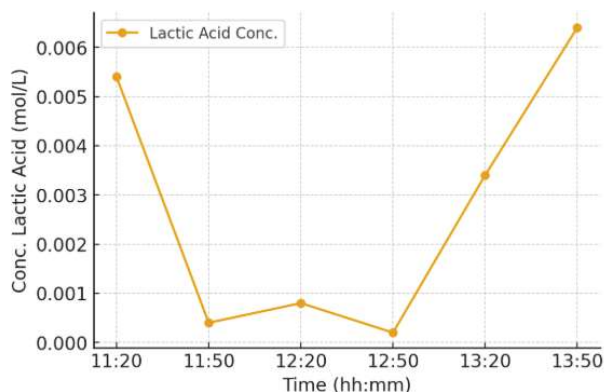


Fig. 3(a). Lactic acid concentration with time

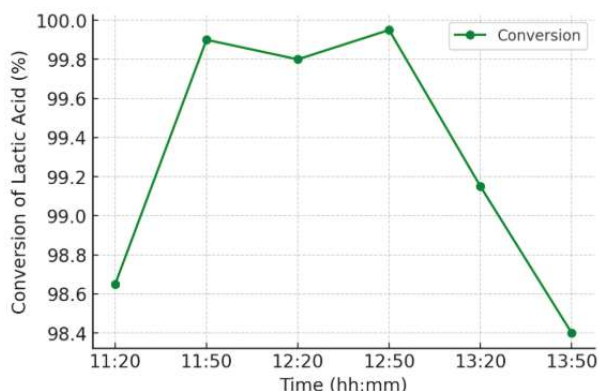


Fig. 3(b). Esterification conversion with time

These graphs clearly show the concentration of lactic acid decreases and the conversion rate increases as the reaction progresses, then fluctuates due to equilibrium shifting. The observed data support the theory that prepared silver sulphate bentonite catalyst accelerated the forward esterification reaction, achieving conversion $> 98\%$. But the reversible nature of the reaction causes a decrease in the concentration of ethyl lactate due to the backward reaction. These limit the conversion and can be prevented by shifting the equilibrium by adding excess ethanol or continuous removal of water.

3.3 Effect of various parameters on reactions :

The results confirm that reaction time, catalyst dosage, and excess ethanol usage are critical parameters that affect the overall rate of esterification reaction.

Reaction Time: It was observed that within the first 60 minutes, there was a rapid increase in the conversion of lactic acid, up to $> 98\%$. Beyond these, fluctuations occurred due to equilibrium shifting. It can be concluded that the catalyst accelerates the forward reaction and also reduces the time required to reach equilibrium compared to a homogeneous catalyst.

Catalyst Loading (5 wt% of lactic acid): At this loading, the catalyst provided sufficient acid sites for increased conversion. In case of higher dosage, the reaction rates are expected to further increase the reaction rate.

Molar Ratio of Reactants: Equimolar basis for performing the reaction was taken as 0.4 M lactic acid and 0.4 M ethanol. Typically, excess ethanol was used to overcome the equilibrium barrier, leading to a higher yield of product.

3.4 Catalyst reusability :

The reusability is an important factor that proves the economic and environmental viability of a catalyst. After completion of the reaction, the solid catalyst was separated by filtration and then washed with ethanol to remove accumulated reactants or products and oven dried.

The catalyst showed retained activity in the first 2 cycles, which then slightly decreased over repeated use. This was due to the blocking of active sites and pores by absorbed reactants and products. The overall result of the experiment concluded that the catalyst is reusable, which increases the process efficiency.

4. Conclusions :

Silver sulphate supported bentonite clay was successfully synthesized and used as a heterogeneous catalyst for the esterification of lactic acid and ethanol to produce ethyl lactate, which is a green solvent and environmentally compatible, and biodegradable. The acid treatment of bentonite clay resulted in the enhancement of the surface area for silver sulphate impregnation. Impregnation of bentonite clay with silver sulphate introduced catalytically active sites, which were analyzed by FTIR.

Titration analysis data showed that the conversion rate of lactic acid was more than 98% with a reaction time of less than 2 hours. Equilibrium shifting caused minor fluctuations at later times that showcased the reversible nature of the reaction.

These results highlight that silver sulphate bentonite catalyst is a reusable catalyst for esterification reaction, aligning with the green chemistry principles that ensure the final product is of high purity. Future studies should focus on advanced characterization, such as XRD, STEM, and BET, for a better understanding of the surface activity of the catalyst and its commercialization.

References :

- [1] Ochoa-Gómez, J.R., Gómez-Jiménez-Aberasturi, O., Maestro-Madurga, B., Pesquera-Rodríguez, A., Ramírez-López, C., Belsué, M. (2012). Synthesis of ethyl lactate by esterification of lactic acid with ethanol catalyzed by ion-exchange resins. *Catalysis Today*, 195: 74–81.
- [2] Bhosale, A., Mulani, K., & Sawant, S.B. (2005). Esterification of lactic acid with ethanol catalyzed by heteropoly acids. *Industrial & Engineering Chemistry Research*, 44(24) : 9114–9119.
- [3] Dussan, K., Giraldo, L., & Moreno-Piraján, J.C. (2016). Esterification of lactic acid with ethanol using ion-exchange resins: Kinetic study and thermodynamic analysis. *Chemical Engineering Journal*, 283: 418–427.
- [4] Benedict, R., Parulekar, S., & Tsai, S. (2003). Esterification of lactic acid and ethanol with/without pervaporation. *Industrial & Engineering Chemistry Research*, 42(11) : 2282–2291.
- [5] Hasegawa, Y., Yamaguchi, K., & Mizugaki, T. (2011). Synthesis of ethyl lactate using solid acid catalysts under solvent-free conditions. *Green Chemistry*, 13(2) : 306–310.
- [6] Zhang, L., Yang, J., & Xu, J. (2004). Kinetics of esterification of lactic acid with ethanol catalyzed by cation-exchange resins. *Reactive and Functional Polymers*, 61(1) : 101–114.