Catalytic Synthesis of n-butyl Acetate over Surface Modified SiO₂ as a Facile Catalyst

Dominic Savio Dias[1], Carolina F. E. Fernandes[2]

[1]Department of Chemistry, P. E. S's R. S. N. College of Arts & Science, Goa-India
Corresponding Author Email: *dominicsaviodias[at]gmail.com*

[2]Department of Microbiology, P. E. S's R. S. N. College of Arts & Science, Goa-India

Abstract: *n-Butyl acetate was being synthesized using SiO₂ whose surface was modified using Nitric acid. The percentage conversion of the acetic acid was found to be ~57% with acid to alcohol mole ratio of 2:1. The catalyst was characterized by FTIR spectroscopy, XRD analysis and PZC value was being determined. Kinetic studies were carried out to determine the order of the reaction and the activation energy which revealed the esterification reaction to be a second order reaction.*

Keywords: Ecofriendly Catalysis, SiO₂, Solid acid, Esterification, Kinetic studies

1. Introduction

Globally there is an urging need for process which occurs by green methods. The best approach in chemistry focusing on green chemistry is by utilizing a solid catalyst in the synthesis. The prime importance of heterogeneous catalysis over homogenous catalysis is that the heterogeneous catalyst is easy to recover, can be reused more than once, is economical; etc.(O.I.Peter et al, 2012)

Ester is a group of organic compounds which are regarded as the derivatives of carboxylic acids. They are normally obtained by reacting an acid with an alcohol via a acid catalyzed reaction as reported by Fisher. Recently, solid acid catalysts are replacing these commonly used mineral acids (A. P. Toor et al,2011). In literature, synthesis of monoesters and diesters is being reported over zirconium (IV) phosphate as a solid acid catalyst (H. K. Patil et al, 2008). Methyl Oelate is being reported to be synthesized over a solid acid (L. M. Z. Tito et al, 2011). Recently, sulfated zirconia is utilized to synthesize an ester of myristic acid and methanol (B. Tyagi et al, 2012). Even the heteropolyacids are reported in the synthesis of esters. (Shanmugam et al, 2004).

n-Butyl acetate is an ester commonly used as an artificial flavoring agent in foodstuffs such as ice- cream candy;etc. It is also used in the manufacture of some plastics, nail care products; etc (K. L. Williamson et al, 1994). Vanadium oxide, Bi₂SO₄, Bismuth, zinc oxide and ion exchange resin is reported to be a solid acid catalyst for its synthesis recently in the literature (G. Mitram et al, 2012; S. Naik et al, 2015; F. R. da Silva et al, 2014).

In the present work, the cheaply available SiO₂ in the form of silica is taken and is impregnated with the protonated acid sited using nitric acid and is used for the synthesis of n-butyl acetate. This method is greener as it does not utilize much of the chemicals for its synthesis and also silica once used is discarded as a waste. And here, we can actually reutilize the discarded silica with a modified surface by impregnating it with the protonated acid sites for the synthesis of n-butyl acetate.

2. Materials and methods

2.1. Materials

Acetic acid and n-butanol were purchased from S. D. Fine chemicals having 99.5% purity. NaOH, KNO₃, KOH and HNO₃ having 99.5% purity was also purchased from S. D. fine chemicals.

2.2 Methods

2.2.1 Surface modification of SiO₂
The SiO₂ n the form of silica was obtained from Rankem Chemicals. It was refluxed with 1M HNO₃ for 4 hours and was filtered and washed with distilled water till the filtrate gave negative test for nitrate. The resulting surface modified SiO₂ was dried in oven at 110^0C for 2.5 hours and was coded as SA. SA was characterized via XRD analysis which utilized CuKα radiation and Ni as the filter.

2.2.2 Determination of Point of Zero charge (PZC)
For the determination of PZC 3mL of 0.1M KNO₃ and 6mL of distilled water was taken in two beakers. To one beaker 50 mg of the SA was added. 0.01M KOH was added in increments of 1mL to the beaker containing the SA (main) and the one without SA (blank) and its pH was recorded using a pH meter.

2.2.3 Pyridine adsorption Studies
The surface acidity was measured using Pyridine adsorption method. Here, 0.1g of SA (activated at 120^0C) was taken and was exposed to the pyridine vapors using a desicator for 4-5 hours and then the SA was dried in an oven at 110^0C and its FTIR spectra was recorded (S. Naik et al, 2015).

2.2.4 Esterification of n-butanol with acetic acid
In a round bottomed flask about 25 mL of n-butanol was charged and to it about 31.2 mL of glacial acetic acid was added and 1.5 mg of SA was added to it and placed on a magnetic stirrer with heater maintained at 80^0C. 1mL of the solution was withdrawn from the reactor and was titrated against 1M NaOH using phenolphthalein as an indicator and the %Conversion of glacial acetic acid was determined as follows (O. I. Peter et al, 2012):

%Conversion of glacial acetic acid$= \frac{[C]i-[C]t}{[C]i}$ x 100

Where, $[C]_i$= initial concentration of glacial acetic acid
$[C]_t$=concentration of glacial acetic acid at time t

3. Results and Discussion

SA when subjected to X-ray diffraction studies in the scanning range of 10^0-80^0 revealed that SA is amorphous in nature as there is no sharp peak which isto be seen. Also, a peak at 22^0 indicates the presence ofSiO₂ phase in SA (as shown in fig. 1), which confirmsthat it is SiO_2. (JCPDS, 72-0514)
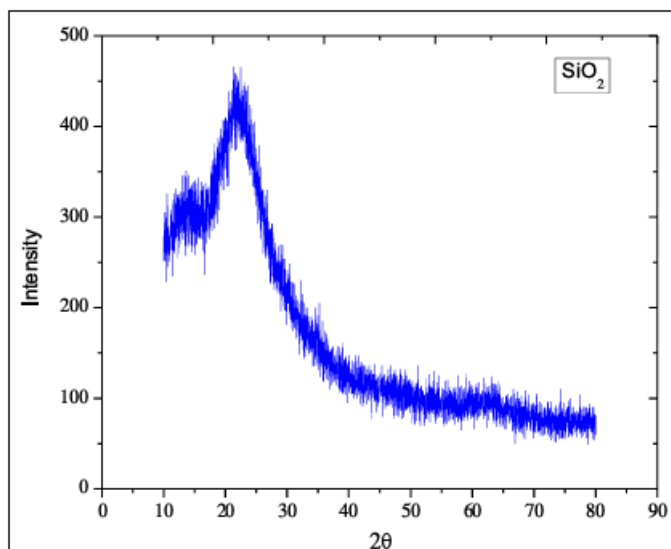
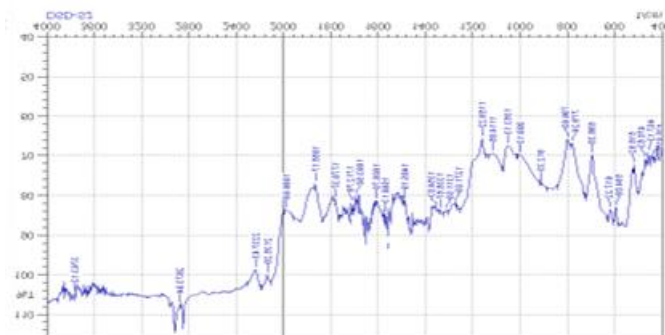**Figure 1:** X-ray Diffraction pattern of SA.

Figure 2: FTIR spectra from Pyridine adsorption studiesof SA.

From Pyridine adsorption studies via FTIR analysis scanned from $400cm^{-1}$ – $4000cm^{-1}$ (fig. 2), the spectra shows the presence of peak between $800cm^{-1}$ to $1086cm^{-1}$ which corresponds to Si-O-Si linkage, apeak at $457cm^{-1}$ corresponds to Si-O stretching. Peak in the range of 1392-$1427cm^{-1}$ corresponds to the presence of Lewis and Brosted acid sites and the sole peak at $\sim1587cm^{-1}$ corresponds to a combination bandof Lewis and Brosted acidic sites.

From the point of zero charge (PZC) studies we see that SA has a PZC value of pH 3 as shown in fig. 3. From this we can say that above pH 3 SA will be a OH^-donor and below pH 3 SA will be a H^+ donor respectively.
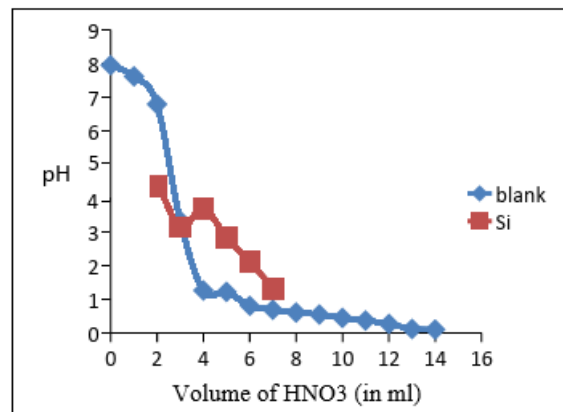

Figure 3: Plot depicting PZC value of SA

Esterification reaction of n-butanol with glacial acetic acid over SA showed ~57% Conversion of acetic acid.This can be attributed to the influence of PZC value ofpH 3. As the pH of the reaction mixture during thereaction was not exceeding the pH 3, we can say thatSA served as a proton donor in the reaction media.Also, as we know that esterification reaction isnormally an acid catalyzed reaction and therefore SAin the pH range of pH 3 must have facilitated the reaction to go in the forward direction. In order to carry out the kinetic investigations the plotsof % Conversion of acetic acid v/s time (in minutes) was plotted and from it ln [A] v/s time (in seconds) for a first order reaction and 1/ [A] v/s time (in minutes)for a second order reaction was plotted at two different temperatures as shown in fig.4, fig. 5 and fig.6 (Here [A] is the concentration of Acetic acid) and the results are summarized in table 1.
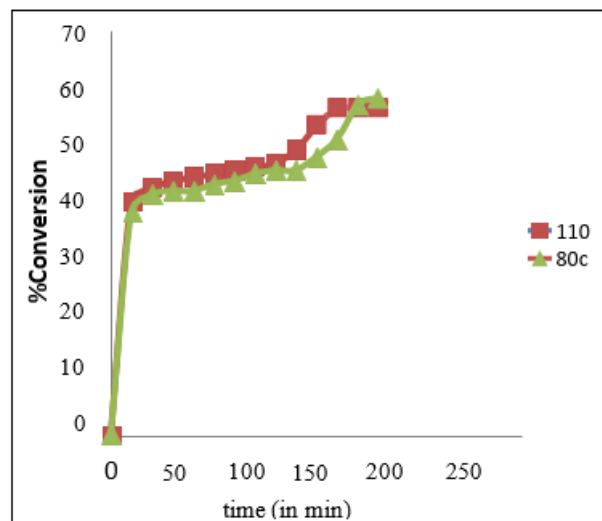

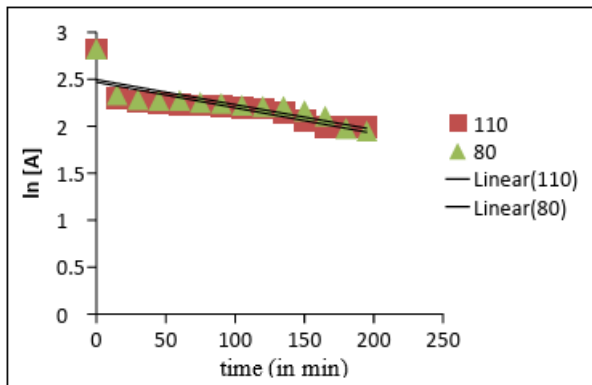**Figure 4:** Plot showing %Conversion of Acetic acid as a function of time.
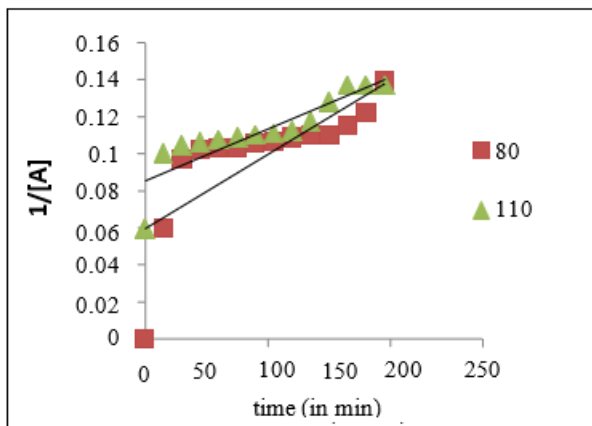
Figure 5: Plot showing ln[A] as a function of time.
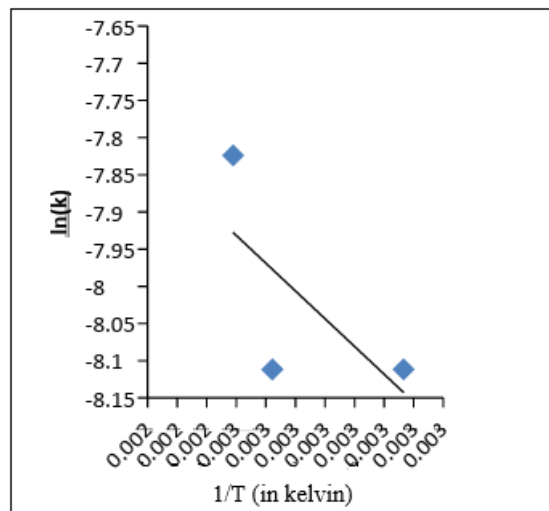

**Figure 6:** Plot showing 1/[A] as a function of time.

Figure 7: Plot showing ln(k) as a function of 1/T

Table 1: Data from the kinetic studies ofesterification reaction of n-butyl acetate

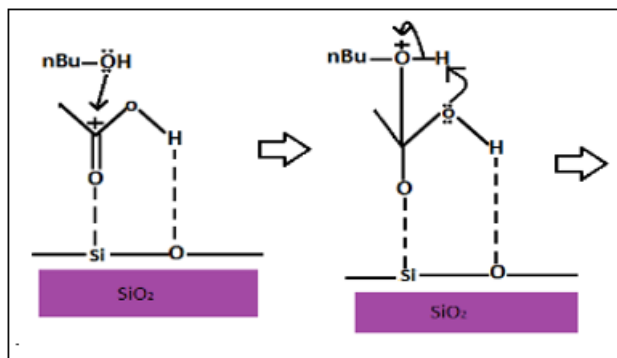| Temperature in °c	First order rate Constant k min⁻¹	Correlation coefficient	Second order rate constant (mol·L sec⁻¹)	Correlation coefficient
80	0.0027	0.676	0.003	0.5894
10	0.0027	0.678	0.003	0.784

From table 1, it is evident that the esterification reaction of n-butanol with acetic acid follows second order reaction kinetics as indicated by its correlation coefficient having the value of 0.7380.

In order to investigate the energy of activation a plot of ln K v/s 1/T (in Kelvin's) was plotted as shown in fig. 7 which indicated the activation energy having the value of ~0.506KJ/Mol.
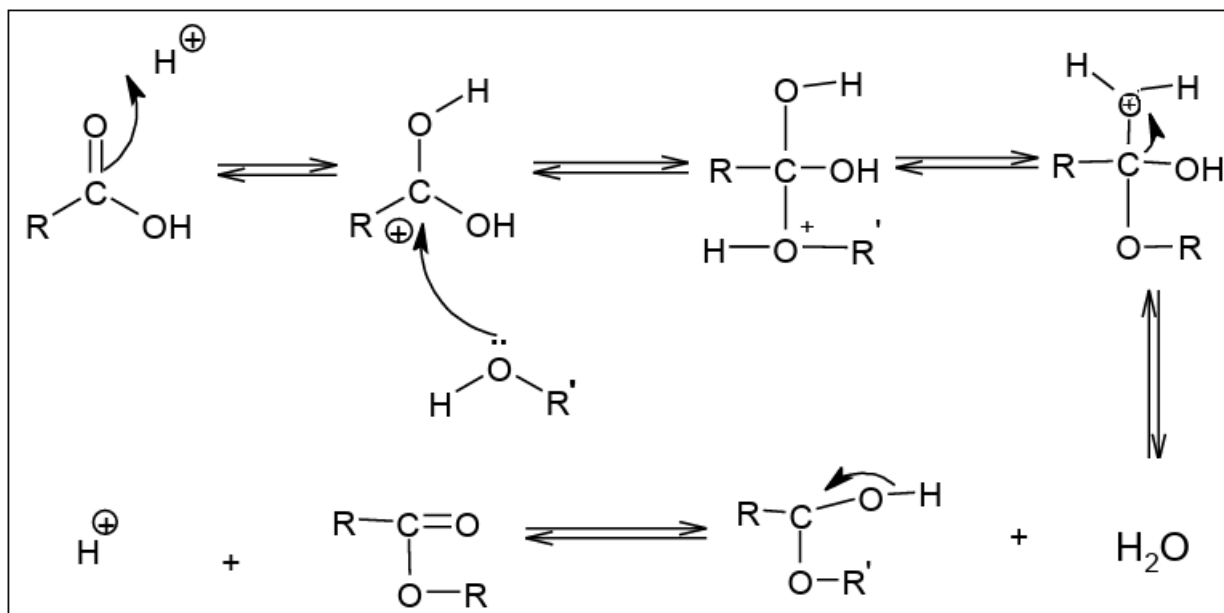
Scheme 1: Plausible mechanism for esterification reaction of n-butyl acetate

The plausible reaction mechanism(O. I. Peter et al, 2012) for the esterification reaction of n-butanol with acetic acid is as shown in scheme 1. And the reaction mechanism according to Eley-Rideal (S. Naik et al, 2015) is as shown in scheme 2.

Volume 13 Issue 3, March 2024
Fully Refereed | Open Access | Double Blind Peer Reviewed Journal
www.ijsr.net

Paper ID: SR231009201227   DOI: https://dx.doi.org/10.21275/SR231009201227   1753

Scheme 2: Proposed Eley-Rideal Mechanism forsynthesis of n-butyl acetate on SA

4. Conclusion

It can be concluded that n-butyl acetate can be successfully synthesized over SA as a solid acid catalyst. In our present investigation ~57%. Conversion of acetic acid was obtained for 1.5g of SA. Kinetic investigations reveals that the esterification reaction over SA followed the second order reaction kinetics having the activation energy of ~0.506KJ/Mol. SA is an ecofriendly and a low cost catalyst which can be used for the production of n-butyl acetate and therefore can be the studied synthesis can be said to be a green synthesis of n-butyl acetate.

References

[1] Amrit Pal Toor et.al ,2011. "Kinetic studies of esterication reaction of acetic acid with n-butanol and iso-butanol catalyzed byionexchage resin." *Bulletin of chemical reactionengineering and catalysis* 23-30.

[2] Beena Tyagi, K. Saravanan. 2012. "Sulfated zirconia: an efficient soild acid catalyst for esterification of myristic acid with short chain of alcohol." *Catalysis Science and Technology* 2512-2520.

[3] Fabiano Rosa da Silva et.al. "Esterification ofafatty acids using Bismuth-containing solid acid catalyst." *Energy and Fuels.1-5*

[4] Gheorghita Mitran, Eva Mako, Akos Redey, Ioan-Cezar Marcu. 2012 "Esterification o acetic acid with n-Butanol using Vanadium oxides supported on γ-alumina." Compts Rendus Chimie."793-798.

[5] H.K. Patel, R. S. Joshi, U.V. Chudasama. 2008. "Use of zirconium (IV) phosphate as a solid acid catalyst in some esterification reaction." *Indian journal of chemistry* 348- 352.

[6] K.L.Williamson. 1994. "Synthesis of n-Butylacetate via Esterification." *Macroscale and Microscale Organic Experiments* 38

[7] Laura M.Z.Tito et.al 2011. "Esterification oleic acid over solid acid catalyst prepared from amazon flint kaolin." *Applied catalysis B: Environmental* 495-503.

[8] okoye ifedi peter, obi chidi et al. 2012. "The preparation and application of environmentally bening titanium pillared clay catalyst for esterification of ethanol and acetic acid." *American Chemical science Journal* 45-59.

[9] S. Shanmugam, B. Viswanathan, T. K. Varadarajan. 2004 "Esterification by solid acid catalysts-a comparison". Journal of Molecular Catalysis A."143-147.

[10] Sajo Naik et.al, 2015. "Zinc oxide as a solidacid catalyst for esterification reaction."*Catalysis communication* 24-27.

Volume 13 Issue 3, March 2024
Fully Refereed | Open Access | Double Blind Peer Reviewed Journal
www.ijsr.net

Paper ID: SR231009201227　　DOI: https://dx.doi.org/10.21275/SR231009201227　　1754