Green Synthesis of n-Butyl Acetate in the Liquid Phase Using Natural Silica as a Novel, Highly Efficient and Stable Catalyst

Abd El-Aziz A. Said*, Mohamed M. M. Abd El-Wahab, Mohamed N. Goda, Nadia O. El-Gamal

Chemistry Department, Faculty of Science, Assiut University, Assiut, 71516 Egypt

E-mail: aasaid55@yahoo.com, a.a.said@aun.edu.eg (Abd El-Aziz A. Said)

Abstract

In this paper, the liquid phase esterification of acetic acid with n-butanol was investigated over natural silica as a novel catalyst. The catalyst was characterized by XRF, XRD, and nitrogen sorption analysis. The effect of different parameters such as reaction time, molar ratio, catalyst dosage and calcination temperature on the esterification reaction was studied. The results show that, natural silica catalyst exhibited excellent catalytic performance with a selectivity of 100% to n-butyl acetate formation and the maximum yield obtained in batch method is 86%. This yield is successfully improved to a higher value nearly to 100% with a reactive distillation column.

Keywords: n-Butyl Acetate; Natural Silica; XRF; XRD.

1. Introduction

Nowadays, there is an increasing interest in the preference of chemical industries toward new routes that should meet supplies such as producing of nearly zero waste chemicals, fewer energy, and sufficient uses of product chemical in various applications [1]. One of these industries is the production of esters via the interaction between acid and alcohol. Such organic esters are principally used in the fabrication of perfumery, plastics, fine chemicals, ……..etc [1]. n-Butyl acetate is a significant ester having widespread requests in the manufacturing [1-3]. Additionally, it is able to substitute the toxic teratogenic ethoxy ethyl acetate, which is often used as a solvent [4].

It is also broadly used in the manufacture of nitrocellulose, perfumes, tastes and numerous products for the medicinal industry [5-8]. The consumption of n-butyl acetate grows in the last two decades because it is of less toxicity and environmental eco-friendly in comparison with other esters [9]. Esterification reactions have been achieved broadly using homogenous and heterogeneous catalysts [10-11]. Typical homogenous catalysts like H_2SO_4, HCl, HF, H_3PO_4, $ClSO_4$-OH,…. etc are generally used in industries [10-12]. For economic and environmental reasons, such as their corrosive effect and the difficulty of their separation, heterogeneous catalysts, such as solid acid catalysts [13-45] become attractive native catalysts. Several solid acid schemes were used in esterification reactions, counting traditional solid acid such as ion exchange resins zeolites, super acids like sulphated zirconia, heteropoly acids (HPA) having the kegging –type structure. However, the benefits of the HPA are more unique due to their low volatility, low harmness, high acidity, activity and elasticity. Unfortunately, the main drawbacks of such HPA as catalysts lie in their relatively low S_{BET} [1-10 m^2/g], low stability and isolating difficulties from the reaction media [26, 27]. On the other hand, the commercially accessible solid acid catalysts have lately been relatively examined in the esterification of acetic acid with butanol [28]. Among these oxides of elements with valence +5 or higher, MoO_3 and V_2O_5 exhibited strong to very strong BrØnsted acidity that makes them good candidates as solid acid catalysts [29]. It has recently been shown that MoO_3/Al_2O_3 and V_2O_5/Al_2O_3 were capable to catalyze the esterification reaction of acetic acid with n-butanol giving conversions of 81% and 63%, respectively, and 100% selectivity to n-butyl acetate at 100°C and a reaction time of 2h [30,31]. Moreover esterification of acetic acid with n-butanol over clay [32] and various SiO_2 supported catalysts, such as SO_4-ZrO_2/SiO_2 [21], MoO_3 / SiO_2 [33], WO_3 / SiO_2 [34] and Nb_2O_5 / SiO_2-Al_2O_3 [35] and others [44, 45] have been reported. As a general, adopting heterogeneous catalysts has the following inherent advantages over catalysts effected by dissolving electrolytes: (i) they eradicate the corrosive mineral acids, (ii) the catalyst can be easily isolated from the reaction blend by filtration or and (iii) the clarity of the products is higher [36-38]. However, to the best of our

knowledge, the utilization of natural silica as a catalyst for esterification of acetic acid with n-butanol has not been examined. Thus, the main object of the current work is to provide a process for the production of n-butyl acetate using local natural silica that obviates the various drawbacks as detailed above. Furthermore, the impact of several factors such as reaction time, reaction temperature, the molar ratio of the reactants and catalyst loading on the n-butyl acetate synthesis were studied to adjust the optimal reaction conditions.

Experimental

1.1. Catalyst preparation and Materials

Natural silica catalyst used was locally sourced. It was collected from the Western desert of Egypt. The obtained sample was dried overnight at $110^{o}C$ and sieved to 0.25 mm and then further calcined at $200^{o}C$. Bio-glacial acetic acid, and bio-butyl alcohol were obtained from the Egyptian Sugar and Integrated Industries Company (Fermentation unit) as pure reagents and were used without extra purification.

1.2. Characterization

The XRF analysis was conducted for natural silica catalyst calcined at $200^{o}C$ (<0.25 mesh) using a Philips X-Ray fluorescence model PW/2404, with Rh radiation tube and eight analyzing crystals. The X-ray diffraction (XRD) of silica sample calcined at $200^{o}C$ was carried out using a Philips diffractometer (Model PW 2103, $\lambda=1.5418$ Å, 35 KV and 20 mA) with a source of $CuK\alpha_1$ radiation (Ni Filtered).
Nitrogen sorption isotherms were measured at $-196^{\circ}C$ using the Quantachrom Instrument Corporation, USA (Model Nova 3200). Test samples were thoroughly outgassed for 2h at $250^{o}C$.

1.3. Catalytic activity

The liquid-phase esterification of CH_3COOH with CH_3-$(CH_2)_2$-CH_2-COOH was performed in a 250 ml glass flask connected with a water-cooled condenser as previously described [39]. The whole volume of the acid and alcohol was kept at 100 ml. The reaction temperature was controlled using a thermostated heating

mantle. The temperature inside the flask was controlled with an accuracy of $\pm 1^{\circ}C$. Tests were planned by varying refluxing time, acid: alcohol molar ratio, catalyst weight, and calcination temperature. Blank reactions were also examined in the nonexistence of a natural silica. The reaction products were evaluated by gas chromatograph with FID detector (proGC Unicam instrument) using a glass column 10% APL (2m). The % conversion was estimated using the manner that earlier defined by Kirumakki et al. [39]:

$$\text{Conversion of n} - \text{butanol}(\%) = (1 - \frac{[\text{Alcohol}]}{[\text{Alcohol}] + [\text{Acetate}]}) \text{ X } 100$$

To gain precise results, each test was evaluated three times.

2. Results and discussion
2.1. Characterizations

XRF analysis data of natural silica catalyst calcined at $200^{\circ}C$ are shown in Table (1). Inspection of these data reveals, the existence of SiO_2 as a main phase together with some traces of other oxides with percentages not exceeded than 2.5%. In addition, Al_2O_3 was found in this sample with some low percentage (1.19%). The data also disclose the presence of some organic matter and/or volatile materials which were lost as presented in Table (1).

Table 1. XRF analysis of natural silica catalyst calcined at $200^{\circ}C$

Oxide	SiO_2	Al_2O_3	Fe_2O_3	SO_3	K_2O	Mn_2O_3	TiO_2	P_2O_5	Loss
Wt. %	97.42	1.19	0.06	0.32	0.21	0.23	0.32	0.09	0.16

Figure (1) shows the XRD patterns of natural silica catalyst annealed at $200^{\circ}C$. Matching the diffraction lines which are located at d (Å) = 4.36, 3.40, 1.83, 1.68, 1.38 and 1.26 with that identified in JCCD (01-089-8941) reveals the presence of the well crystalline quartz (α-SiO_2). In addition, no other peaks were observed for the other components of the sample like Al_2O_3, Fe_2O_3, …..etc, which may be attributed to their low concentration to be detected by XRD.

Nitrogen adsorption-desorption isotherm of natural silica calcined at $200^{\circ}C$ was measured at the temperature of liquid nitrogen

(-196°C) and is shown in Fig. (2). Examination of Fig. (2) revealed that, the isotherm is of type II of Brunauer's classification [46]. In addition, it is characterized by being irreversible and exhibit hysteresis loop close in the low relative pressure range. The observed hysteresis loop belongs to type H3 with little of H4 of de Bore classification [47]. These results may indicate primarily that we deal essentially with plate-like aggregates giving slit-like shaped pores.
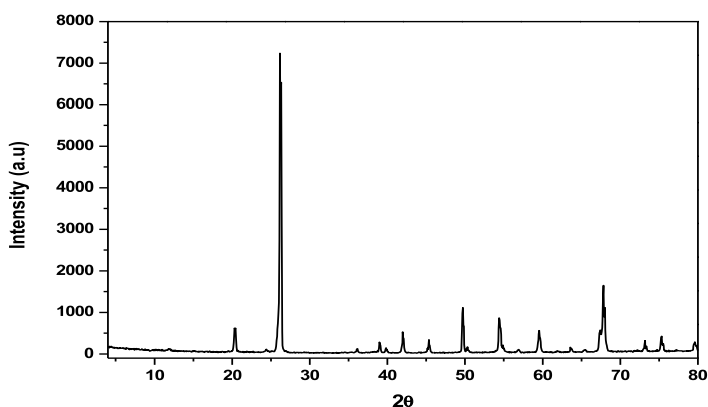

Fig. (1): X-ray diffractogram of natural silica catalyst calcined at 200°C

On the other hand, the specific surface area calculated from the BET theory, $S_{BET,}$ was obtained by adopting the BET equation in its normal range of applicability (p/p$_o$ =0.05 − 0.30) with a cross-sectional area of N$_2$ molecule of 16.2 Å^2. The BET linear plots permit the calculation of monolayer capacities (V$_m$) from which the S$_{BET}$ can be calculated.

The computed S$_{BET}$ value of natural silica calcined at 200°C is 3.4 m^2 g^{-1} with a value of total pore volume of 7.3 cc g^{-1}.

To shed a light on the porosity of these catalysts, the volume thickness plots (V$_a$-t) and pore size distribution curves should be constructed.

The V$_a$-t plot of natural silica catalyst is drawn and not shown here. This plot was created adopting de-Bore method depending on the magnitude of C-constant of the BET-equation. From examination of this plot, one can observe that the V$_a$-t plot exhibit upward deviation indicating a mesooporous nature of the existing pores [46].

To confirm this mesoporosity exhibited by natural silica, the pore volume distribution curve was plotted and shown in Fig. (2). Examination of this figure revealed that only one peak (at 3.9 nm) maximized in the mesoporous region indicating that mesopores are present.
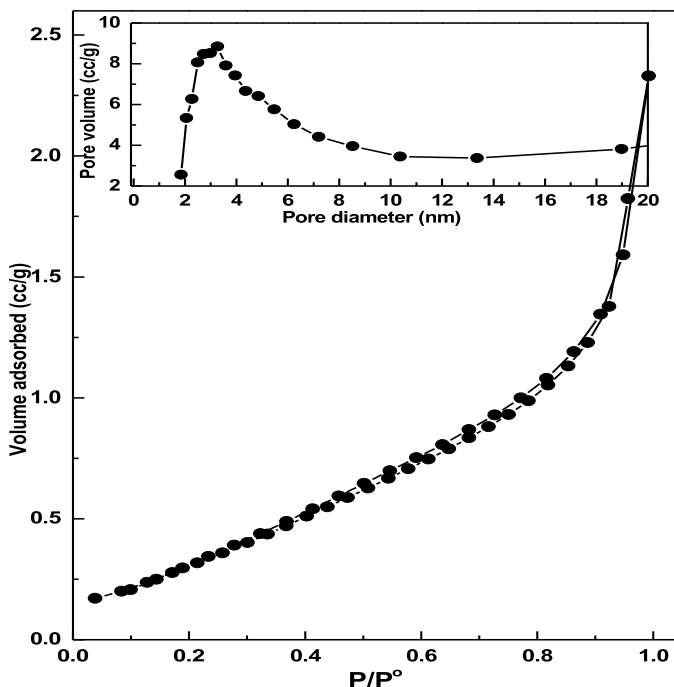

Fig. (2): Nitrogen adsorption-desorption isotherm and pore size distribution curves of natural silica catalyst calcined at 200°C.

2.2. Catalytic activity

The liquid-phase esterification of acetic acid with n-butanol experiments was conducted in a batch to observe the effects of various parameters on the catalytic activity of the natural silica. These factors are namely, refluxing time, the initial molar ratio of reactants, reaction temperature, catalyst loading, calcination temperature and reusability. These factors are studied below:

2.2.1. Effect of reaction refluxing time

The impact of reaction refluxing period on the catalytic esterification reaction of acetic acid with n-butyl alcohol over 0.5 g

of natural silica calcined at 200°C was studied at different refluxing time up to 5 h while the alcohol : acid molar ratio is kept constant at 1:2 and at 110°C. The attained results are painted in Figure (3). These results can be concluded as the following points: (i) the % conversion of n-butanol and % yield of n-butyl acetate monotonically increase with growing up of the refluxing time up to 3 h. Upon further increase of reflux time, no weighty increase in the catalytic activity was noticed. This means that 3h is a sufficient time to attain top conversion and selectivity, and the selectivity of catalysts towards n-butyl acetate formation was 100%.

2.2.2 Effect of acid: alcohol molar ratio

The impact of the alcohol to acid molar ratio on the esterification of acetic acid with n-butanol in the occurrence of natural silica catalyst calcined at 200°C was conducted over 0.5 g catalyst, at 110°C and after a refluxing time of 3h and the data obtained are presented in Figure (4). As observed, the conversion and yield of n-butyl acetate increase upon increasing the molar ratio of acetic acid, reaching a maximum at the ratio of 1:2, alcohol to acetic acid. Exceeding this ratio to reach 1:3, no significant improvement was noticed in the catalytic activity. Such a behavior may be due to dilution of the alcohol by extra acetic acid, thus avoiding its convenience for neuclophilic reaction with chemisorbed acetic acid [40, 41].
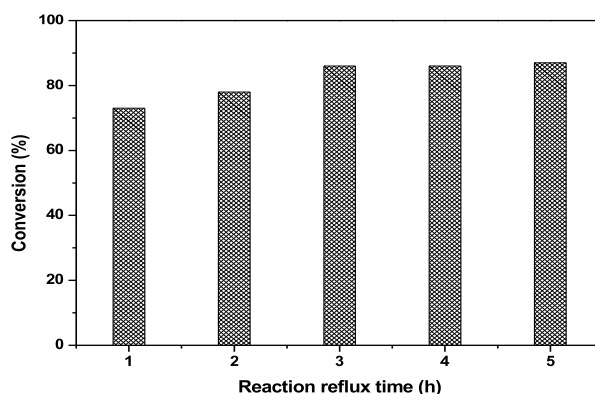

Fig. (3): Effect of reaction refluxing time on the catalytic esterification of acetic acid with n-butanol over natural silica catalyst calcined at 200°C.

2.2.3. Effect of catalyst charging.

The effect of catalyst dose from 0.1 to 2 g on the reaction of acetic acid with n-butanol was examined in existence of natural silica catalyst calcined at 200°C under conditions of a ratio of alcohol to acid at 1:2, a reaction temperature of 110°C, and a refluxing time of 3h. The found results are described in Figure (5). The results revealed that, with the catalyst amount increases from 0.1 to 0.25 g, conversion of n-butyl alcohol increases, while a further raise in the catalyst weight from 0.25 to 2.0 g have almost the same conversion (83-86%). The ideal charging can be taken as 0.25g. The results also demonstrate that even the loading of the catalyst increases, a insignificant increase in the yield of n-butyl acetate was noticed. Such behavior may be ascribed to the effect of hydrophobicity of n-butyl alcohol which could be decreased by the raise in the catalyst weight [40].

2.2.4. Effect of reaction reflux temperature.

The influence of reaction temperature on the catalytic esterification of acetic acid with n-butanol was investigated in the range of 80-130°C without altering other parameters and the data are given in Figure(6). Investigation of this figure revealed that, as the reaction temperature increases from 80 to 100°C, the % conversion increases from 70 to 86%. An extra growth in the reaction temperature almost has the same conversion keeping the selectivity to n-butyl acetate kept at 100%. Such a behavior suggests that the reaction temperature helps creation of carbonium ion form of n-butyl alcohol, which further reacts with acetic acid to form n-butyl acetate [9, 39, 41].
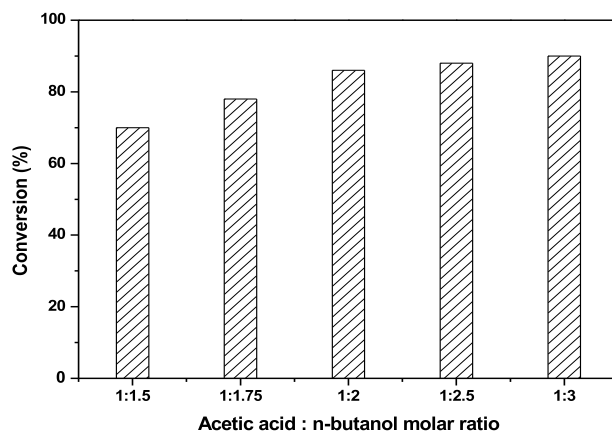
Fig. (4): Effect of acid:alcohol molar ratio on the catalytic esterification of acetic acid with n-butanol over natural silica catalyst calcined at 200°C.
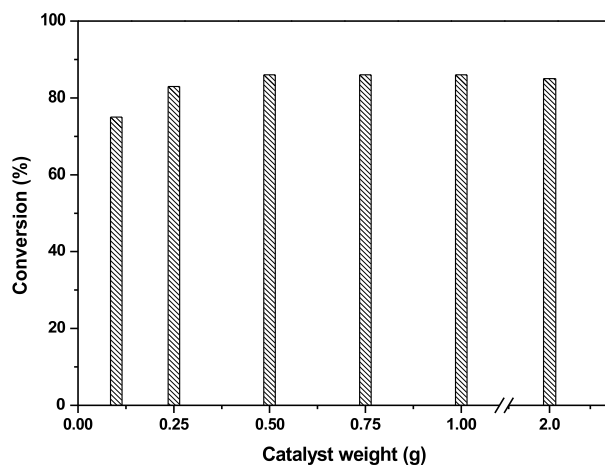

Fig. (5): Effect of weight on the catalytic esterification of acetic acid with n-butanol over natural silica catalyst calcined at 200°C

2.2.5. Effect of calcination temperature

The influence of calcination temperature (200-600°C) on the catalytic performance of natural silica catalyst was tested without altering the other parameters, and the attained results are described in

Figure (7). Close inspection of these results indicates that the calcination temperature has almost no effect where all calcined samples exhibited almost similar conversions within the range of 84.5-87%. Such results reflect that the number of acid sites responsible for the esterification reaction does not altered by the heat treatment of natural silica. Actually, this is a strong point of the local natural silica as a solid acid catalyst to be industrially used in n-butyl acetate formation, besides its large availability in nature, eco-friendly, low cost and easy transportation to factories.

The activation energy (ΔE) of the esterification of acetic acid with n-butanol was also calculated by plotting the value of ln k versus 1/T (Figure (8)), adopting the Arrhenius equation [9]. k is the specific rate constant (min^{-1}) estimated from the plot of ln (1- conversion) against time. The estimated value of ΔE is 11.7 kcal mol^{-1}.

2.2.6. Recycling of the catalysts

The gains of solid catalysts compared with homogeneous acids are their easy recovery and good reusability. In addition, the ability of catalysts to be recycled and reused is a significant factor. So, it is quite necessary to investigate the reusability of natural silica catalyst calcined at 200°C and further reused in the esterification reaction at the same reaction conditions as mentioned above. The recovery process was done as follows: after the 1st catalytic run, the solid catalyst was filtered off, washed several times by bidistilled water, dried at 110°C then used in a fresh reaction mixture of esterification reaction. The above mentioned procedures were repeated in a 3rd and 4th reaction tests and the results are displayed in Figure (9). It revealed that, after four cycles, the yield of n-butyl ester slightly decreases by about 3 %, while the selectivity to ester still remains at 100%. This conclusion allows drawing that this natural silica catalyst is more structured stable with a great improvement of the leaching-resistance property.
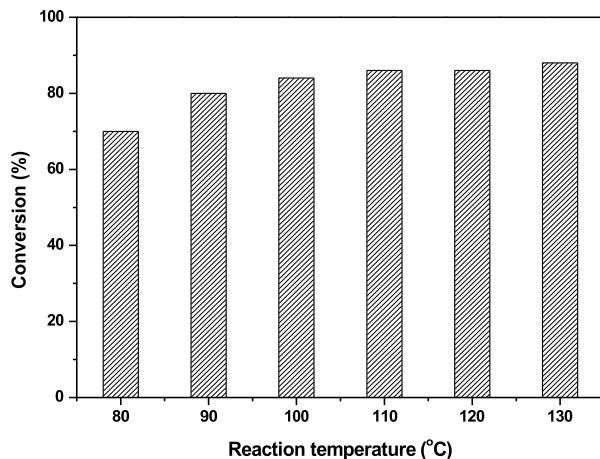
Fig. (6): Effect of catalytic reaction temperature on the catalytic esterification of acetic acid with n-butanol over natural silica catalyst calcined at 200°C.
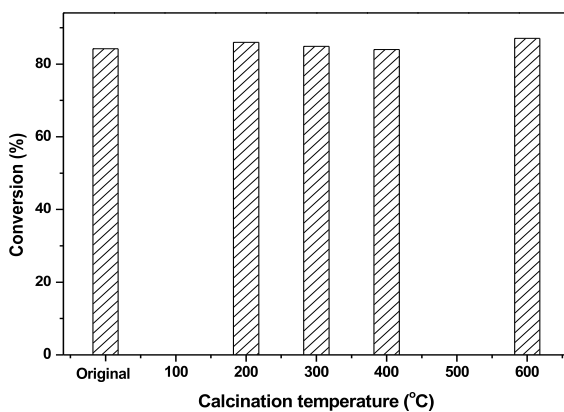

Fig.(7): Effect of calcination temperature on the catalytic esterification of acetic acid with n-butanol over natural silica catalyst.
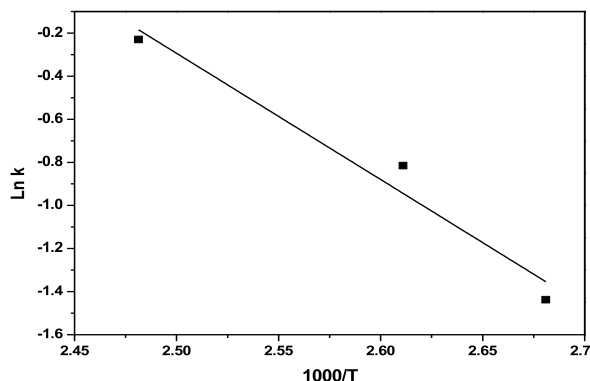
Fig. (8): Arrhenius plot of esterification of acetic acid with n-butanol over natural silica catalyst.

From the optimized conditions, it is clear that the maximum attained yield of n-butyl acetate in batch method was 86 % with selectivity of 100%. To improve this value, the reaction mixture after 3 h of refluxing undergoes a simple distillation and the data are illustrated in Figure (10). Close inspection demonstrated that the obtained yield of n-butyl acetate is greatly improved to reach 99.5%.

Finally a comparison between the current work with that formerly stated in the literature [21, 35-37] is shown in Table (2). Examination of this table demonstrated that our results at least have two advantages. Firstly, n-butyl acetate obtained in this study is higher than that supported catalysts [21, 36, 37] and comparable with that reported by Braga and co-workers [35]. Secondly, the natural silica catalyst underwent up to four cycles and always displaying consistent activity.
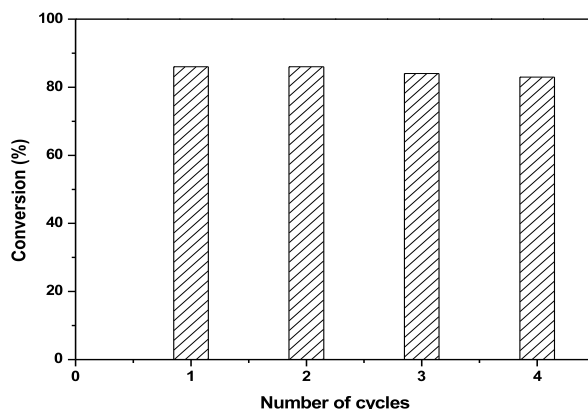
Fig. (9): Recycling of natural silica catalyst calcined at 200°C at a reaction temperature of 110°C.

Table 2. Esterification of acetic acid with n-butanol over natural silica and different supported silica catalysts

Catalyst	Alcohol:Acid molar ratio	Reaction temperature^{o}C	Yield of n-butyle acetate (%)	Reference
5 wt.% MoO_3/SiO_2	1:2	110	80	36
SO_4-ZrO_2/ SiO_2	0.86:1	115-120	66	21
10 wt.% WO_3/ SiO_2	1:2	100	67	37
Nb_2O_5/ SiO_2-Al_2O_3	1:2	120	87	35
Natural SiO_2	1:2	110	86	Present work

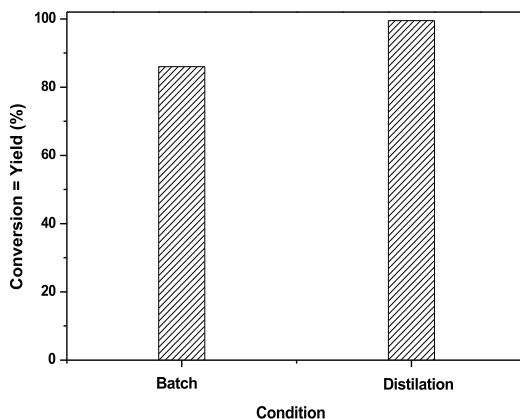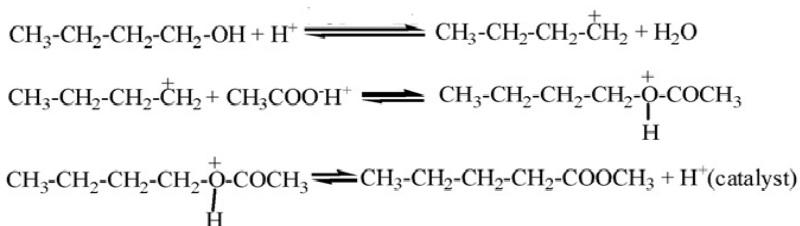**Fig. (10): Yield of n-butyl acetate from batch and distillation conditions**

2.2.7. Reaction mechanism

According to literature [9, 41-43] the esterification of acetic acid with n-butanol is well known as an electrophilic substitution reaction and catalyzed by strong Brønsted acid sites. In addition, it gates according to a rate equation which is a 1st order to acetic acid and 0th order with to n-butanol. Moreover, this reaction is a slow one and can be accelerated either by increasing the reaction temperature or using an active solid acid catalyst. Furthermore, this reaction follows Eley-Rideal mechanism which can take place as follows: (i) formation of carbonium ion via the interaction between the alcoholic OH and the acidic proton of natural silica catalyst originating from the Brønsted OH group over its surface, (ii) formation of unstable intermediate via the attack between the nuclophilic center of acetic acid and the previously formed carbonium ion, and (iii) dissociation of the formed intermediate via removal of H^+ to form n-butyl acetate in company with restoration of the catalyst.

Conclusions

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH + H^+ \rightleftharpoons CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{C}H_2 + H_2O$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{C}H_2 + CH_3COO^-H^+ \rightleftharpoons CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{\underset{H}{O}}\text{-}COCH_3$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{\underset{H}{O}}\text{-}COCH_3 \rightleftharpoons CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOCH_3 + H^+(catalyst)$$

From the above results, the following conclusions can be drawn as follows:

- XRF analysis showed that the natural silica contains SiO_2 as a major phase (97.4 %), and 1.2% Al_2O_3 together with other traces of elements.
- The natural silica catalyst is an active and selective catalyst towards the esterification of acetic acid with n-butanol.
- The supreme conversion, yield and selectivity obtained over natural silica catalyst calcined at 200^oC are 86, 86, and 100% respectively.
- Fewer quantity of catalyst, 0.25 g, and low reaction refluxing period, 3h, are sufficient to obtain n-butyl acetate with a yield of 86%. This yield was greatly improved to reach 99.5% with simple distillation.
- Recycling of natural silica catalyst gave the same activity where only about 3 % loss of its activity after four times using.
- Natural silica under investigation is an excellent candidate where it can be utilized as natural, available, eco-friendly and cheap catalyst for esterification of acetic acid with n-butanol.

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الملخص العربي

تحضير خلات البيوتيل بالطريقة السائلة باستخدام السيليكا الطبيعية كحافز جديد ذو ثبات وكفاءه عالية وصديق للبيئة

عبد العزيز أحمد سعيد- محمد محمود عبد الوهاب- محمد نادى عبد الحميد-
ناديه محمد أحمد عمر

قسم الكيمياء– كلية العلوم – جامعة أسيوط – مصر

فى هذا البحث تم دراسة أسترة حمض الخليك بواسطة كحول البيوتانول فى الحالة السائلة مستخدما السيليكا الطبيعية كعامل حفاز جديد. تم توصيف العامل الحفاز باستخدام حيود وتنويرالاشعة السينية وكذلك امتزازغازالنيتروجين. أيضا تم دراسة تاثيرالعوامل المختلفة التى تؤثرعلى عملية الأستره مثل زمن التفاعل والنسبة المولارية بين الحمض والكحول ودرجة حرارة تحميص العامل الحفاز. وقد أوضحت النتائج أن السيليكا الطبيعية لها نشاط حفزى ممتاز تجاة تكوين خلات البيوتيل بدرجة تحول وناتج 86% وبانتقائية100%. وقد وجدأن هذه الكمية من الناتج يمكن أن تصل تقريبا الى100% باستخدام تقنية التقطير البسيط.