

Tungsten trioxide modified zeolites based catalysts for the esterification of lactic acid: The effect of Si/Al ratio and WO₃ loadings

Nekkala Nagaraju¹, Koppadi Kumaraswamy², Seelam Prem Kumar³, Mitta Harishekar⁴, Satya Kamal Chirauri⁵, Gijnuppali Srinivasrao*⁶, Balla Putrakumar*^{1,7}

¹*Catalysis division, CSIR-Indian Institute of Chemical Technology, Hyderabad, Telangana 500007, India.*

²*Teegala Krishna Reddy Engineering College (TKREC), Hyderabad, Telangana 500097, India.*

³*Sustainable Chemistry Research Unit, Faculty of Technology, University of Oulu, P.O. Box 4300, 90014, Finland*

⁴*Laboratory of Chemical Technologies, Ghent University, Zwaijnarde 9052, Belgium*

⁵*Micron Technology Operations LLP, Hyderabad, Telangana, India, 5000081.*

⁶*Department of Applied Science, University of Technology and Applied Science, Muscat-74, Sultanate of Oman.*

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**Corresponding authors:*

Email: srinivasrao.ginjupalli@hct.edu.com; bputrakumar@yahoo.com

Abstract

Zeolite-supported tungsten oxide catalysts was studied in the gas phase esterification of lactic acid with alcohols in different reaction conditions. Two different types of zeolite pore topology and acidity strength was investigated. The Y & mordenite zeolites supported catalysts was prepared by wet impregnation method by varying the Si/Al ratios in Y-zeolites (Si/Al =), and mordenite (CBV-20A). The X-ray diffraction and FT-IR spectroscopy was examined the phase analysis with a degree of crystallinity and modes of different chemical bonds and compounds existed in the zeolites. The textural and total support acidity properties were evaluated by the N₂ sorption isotherms and ammonia temperature-programmed desorption (NH₃-TPD) techniques. The type of alcohol reactant,

WO₃ loadings and the SiO₂/Al₂O₃ ratio had a profound effect on the esterification reaction performance. The Y zeolites with different SiO₂/Al₂O₃ ratios exhibited varied total acidity and activities. Over 10 wt.% WO₃ loaded Y-zeolite with SiO₂/Al₂O₃ = 60 was found to be the most promising catalyst in terms of high activity and selectivity in lactic acid esterification by butanol reactant. The optimized reaction conditions were determined over the most selective 10W-760 catalyst and at 175 °C temperature with feed molar ratio of 1:3 (Lactic acid to butyl alcohol ratio), and flow rate of 1.0 mL/h, a highest butyl lactate yield and selectivity was obtained. . Over 10 wt.% WO₃ Y-zeolite catalysts exhibited both optimal amount of weak and moderate acid sites, which play an important role in the selective formation of butyl lactate However, the strong acid sites enhance the selectivity of the secondary reactions, which led to the byproducts formation and thus, decreases the selectivity of butyl lactate.

Keywords: *Esterification, Lactic acid, Y-zeolite, Tungsten oxide*

Introduction

Sustainability development goals (SDGs) are important initiatives proposed by UN to achieving better world for the future and current living entities by combating the earth's serious problems that we are facing today such as climate change, energy security, air and water pollution. For chemicals and intermediates manufacturing, more environmentally friendly production methods are critical. Although fossil-based raw materials are predominantly used since 70's, the bio-based refineries are becoming more promising due

to environmental benefits. Nevertheless, to make economically viable, there are several hurdles in the development of processes and catalysts design. One promising way to turn biomass into more sustainable fuels, intermediates, and fine chemicals is to develop an efficient catalytic system by promising techniques [1].

Lactic acid (LA) is a key bio-based building block and an important commodity molecule that can be produced chemically or biochemical process by fermentation using versatile renewable feedstocks [2-3]. LA is utilized in a many industrial sectors such as in food, pharmaceutical, and cosmetic ingredients, preservative and as a flavoring agent. It is well-known, LA is used in producing duce biodegradable polymers e.g., polylactate [4]. There are several ways to synthesize lactic acid from starting bio-based molecules, which includes many process steps i.e., dehydration, dehydrogenation, condensation, reduction, decarbonylation, esterification, and polymerization, all of which require bi-functional (-OH, -COOH) lactic acid molecule. Lactic acid further processes to produce renewable LA esters via esterification reaction. [5]. When lactic acid reacts with various alcohols, corresponding lactate esters are produced in a reversible condensation reaction process. Further, its ester derivatives, such as isobutyl lactate and n-butyl lactate are also widely utilized in artificial sweeteners, emulsifiers, and solvents due of their unique properties [6-9]. The Food and Drug Administration (FDA) added ethyl and butyl lactates to its list of Generally Regarded as Safe (GRAS) directive as a food additives.

Studies on the esterification of LA using homogeneous, heterogeneous, and enzyme-based catalysts have been investigated extensively [8-14]. However, esterification of lactic acid with alcohols is an acid-catalyzed reaction, different inorganic mineral acids such as H_2SO_4 , HCl, H_3PO_4 , or organic acids, such as p-toluene sulfonic acid, are often

used to accelerate the process. The reaction of lactic acid with n-butanol to produce n-butyl lactate has been catalyzed over an acidic cation-exchanged resins [15]. An acidic anion-exchanged resin is very active in catalyzing such reaction, but the temperature effect limits in reaching high LA conversion rate close to equilibrium. Catalytic active sites on resin surface and temperature stability factors play an important role in catalyst life. The research community is focused on developing solid acids which is environmentally benign and stable in LA esterification. Indeed, homogenous catalysts are often used in industries for economic reasons. In homogenous esterification process, several issues arise in terms of environmental concerns, difficult in separation and recovery and thus, hazardous waste generation, handling and specialized ingredients [16].

Taking the environmental risks into account, the most explored catalysts in esterification reactions are heterogeneous solid acid-based catalysts such as zeolites and metal oxides. Li *et al.* studied the mixed metal oxides *i.e.*, $\text{TiO}_2\text{-ZrO}_2$ [17] and $\text{TiO}_2\text{-Al}_2\text{O}_3$ based catalysts [18] in esterification reaction and concluded that the specific surface area and surface acidity are key properties in gaining the highest activity in terms of conversion and selectivity. Most of the reports on lactic acid esterification have been utilizing ion-exchange resins as catalysts prepared by the pervaporation method [12,13,19]. Acid catalysts made of tungsten oxides [20] are employed in different industrial applications, including refineries, petrochemicals, pollution control, and value addition processes in biomass refineries. The active component of tungsten oxide phase play an important role in the overall catalytic performance of the catalysts. For long life and enhanced catalytic activity in acid-catalyzed processes, the active phase of tungsten oxide supported catalysts is also influenced by the phase variation, nature, and support structure. In addition, Y-

zeolites are excellent support materials for the high thermal stability and dispersion of active metal oxides phase owing to their large specific surface area. The impregnation of diverse metal oxides into zeolites provides better interaction between the host and guest, which lead to the formation of useful bifunctional materials for the wide range of applications [21]. Hence in this present study, we synthesized zeolite based catalysts with different loadings of tungsten trioxide (WO_3) as an active phase incorporated into Y and mordenite zeolites. The Y zeolite is prepared with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and studied in the lactic acid esterification with butanol. We prepared and characterized different zeolites and WO_3 supported on Y-zeolite catalysts by changing the Si/Al ratio as well as WO_3 active phase content on support material to tune the desired acidity to catalyze esterification reaction of lactic acid with n-butanol in vapour phase reactor.

Experimental

Catalyst synthesis

The tungsten oxide (WO_3) supported on Y-zeolite and mordenite-based catalysts has been synthesized by the wet impregnation method. In a typical synthesis, ammonium metatungstate hydrate ($\text{H}_{26}\text{N}_6\text{O}_{40}\text{W}_{12}\cdot x\text{H}_2\text{O}$) from Aldrich chemicals was used as a tungsten precursor. Different commercial zeolites were used in this work and denoted with codes: namely CBV-400, CBV-720, CBV-760 are Y-zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and CBV-20A (mordenite) by varying the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios = 5.1, 30, 60 and 20 (from Zeolyst International), respectively. The required amount of aqueous ammonium metatungstate hydrate was used as a precursor to wet impregnate the zeolite support to achieve the nominal WO_3 loadings with 5, 10, 15 and 20 wt.%. The excess amount of water was removed *via* evaporation by continuous stirring at 40°C after zeolites were introduced.

Finally, the aqueous gel was completely dried at 100 °C for 12 h followed by the calcination in air at 550 °C for 4 h in a muffle furnace oven. Two series of WO₃ supported zeolite catalysts have been prepared by the impregnation method. One with 10 wt.% WO₃ supported on Y-zeolite and mordenite supports, namely 10W-400, 10W-720, 10W-760 (WO₃ modified Y zeolites) and 10W-20A. The second series is with different loadings of WO₃ supported on zeolites CBV-760 (SiO₂/Al₂O₃ ratio = 60), namely 5W-760, 10W-760, 15W-760 and 20W-760.

Catalyst characterization

The catalysts were characterized by several techniques to understand the structural and textural properties i.e., surface acidity, pore size distribution, specific surface area, morphology and vibrational modes of specific functional groups using NH₃-temperature programmed desorption (NH₃-TPD), N₂ physisorption, X-ray diffraction and Fourier Transform Infrared Spectroscopy (FT-IR) techniques, respectively.

The powder X-ray diffraction measurements were employed on a Rigaku Corporation (Japan) Ultima IV diffractometer utilizing Ni filtered Cu K radiation (1.5406 Å) at 40kV and 30mA. The measurements were taken at a scanning rate of 5°/min at 2θ = 10° - 80°. FT-IR analysis was performed on a Bruker TENSOR 27 spectrometer using self-supporting discs of a powder dispersed in KBr were recorded at room temperature in the range of 400-3500 cm⁻¹. The N₂ physisorption was performed using Autosorb-1C device (M/s. Quantachrome Instruments Corporation, USA) automated with surface area and pore size analyzer. The catalyst was activated by degassing for around 4 h at 120 °C before the analysis. After degassing, N₂ adsorption-desorption was carried out at -196 °C, with a relative pressure range of 0.05-0.3 p/p°. The BET and BJH methods were used to determine the specific surface area and pore size distribution.

NH₃-TPD experiments were conducted on an AutoChem 2910 instrument (Micromeritics). Prior to TPD analysis, the sample was pretreated with high purity helium flow (50 mL/min) at 300 °C for 1 h. After pretreatment, the sample was saturated with 10 vol.% NH₃ in He mixture (75 mL/min) at 80°C for 1 h and then subsequently flushed with He at 150 °C for 1 h to remove the physisorbed ammonia was performed. TPD analysis was carried out from ambient temperature to 700 °C at a heating rate of 10°C/min. The amount of NH₃ desorbed is calculated using GRAMS/32 software at elevated temperatures.

Catalytic reaction

The esterification of lactic acid with butanol under vapour phase conditions was investigated over the tungsten oxide modified zeolite catalysts at atmospheric pressure. The WO₃ supported zeolite catalyst (300 mg, 20-40 mesh) was diluted with glass beads and packed in the middle of the reactor (30 cm length and 9 mm i.d.) using quartz wool. Initially, the catalyst was pretreated at 250°C for 2 h under nitrogen flow (30 mL/min). Prior to the reaction, a 1:3 mole ratio of lactic acid to butanol solution was introduced into the reactor over the catalyst bed parallel to nitrogen flow (30 mL/min). The liquid products were condensed by an ice-water trap and were analyzed by a GC-MS (Shimadzu GC 2014 equipped with DB-wax column, 30 m × 0.32 mm) connected to a flame ionization detector (FID). The HP-5973 quadruple GC-MSD equipped with an HP-1MS capillary column (15 m × 0.25 mm) was used to confirm the liquid products. The most common products detected were butyl lactate (BL), di-butyl ether, butanol, and unreacted lactic acid, respectively, in GC-MS. Therefore, the discussion on the results of activity is based on the observed conversion (%), yield (%) and the selectivity (%) of butyl lactate is calculated according to the following equations:

LA conversion (%) = (moles of LA consumed / moles of LA in the feed) × 100

Product selectivity (mole %) = (moles of C atoms in the specified product/moles of C atoms in LA consumed) × 100

Yield = (LA conversion × specified product selectivity) / 100 The carbon balance was verified in each experiment to confirm the experimental accuracy with under ±5% error.

Characterization results

X-ray diffraction analysis

Figures 1a and 1b represent the XRD patterns of WO₃ with different loadings on CBV-760 and 10 wt.% WO₃ modified zeolites Y and mordenite, respectively. The corresponding Y zeolite peaks are found at around 2θ values of 10.9, 16, 19, 20, 24, 27, 31, and 32° were observed in all XRD patterns [22]. XRD analysis of the synthesized WO₃ supported on Y-zeolite (CBV-760) (Figure 1a) revealed that after the WO₃ incorporation, no substantial changes were noticed in the Y-zeolite structure. This is probably due to the high dispersion of WO₃ over the surface than in bulk. However, the peaks (2θ = 10.9, 20, 27, and 31°) intensities of the samples were found to be lower than the parent Y-zeolite (CBV-760), revealing the gradual loss of crystallinity caused by the WO₃ deposition over zeolite structure [23]. At lower WO₃ loadings (below 15 wt.%), there are no significant peaks were found related to the WO₃ oxide species over the zeolite surface. However, the increase of peak intensities at 2θ = 23.6° and 33.3° corresponds to the formation of highly crystalline phases at higher loadings of WO₃ (over 15 wt.% samples) [19,20]. The results further confirm that the high dispersion of tungsten oxide species over zeolite surface was observed for 5 and 10 wt.% WO₃ Y-zeolite samples (CBV-760). Furthermore, it is evident that the Y-zeolite structure was intact and not affected by the WO₃ incorporation [24].

Fig.1b represents the XRD patterns of 10 wt. % WO_3 supported on different Y-zeolites and mordenite. It can be seen from XRD patterns that all the samples retained their original zeolite structures, suggesting that the WO_3 was well dispersed onto the zeolite surface [25].

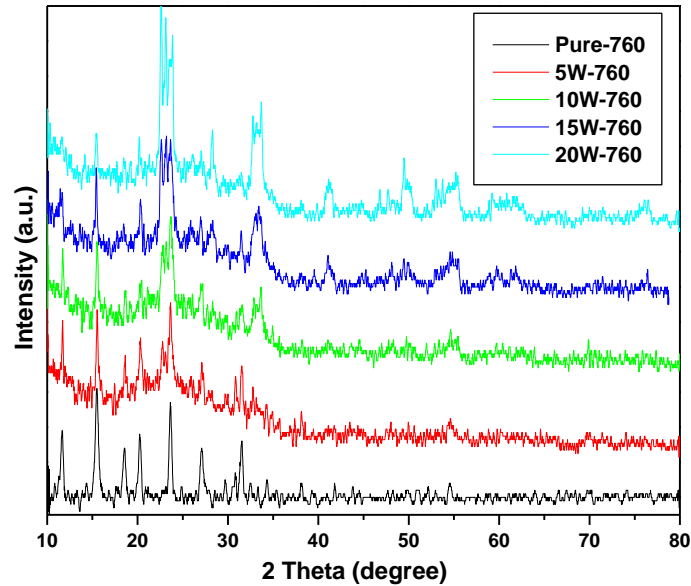


Figure 1a. X-ray diffraction profiles of various WO_3 loadings (5-20 wt.%) supported on Y-zeolite (CBV-760).

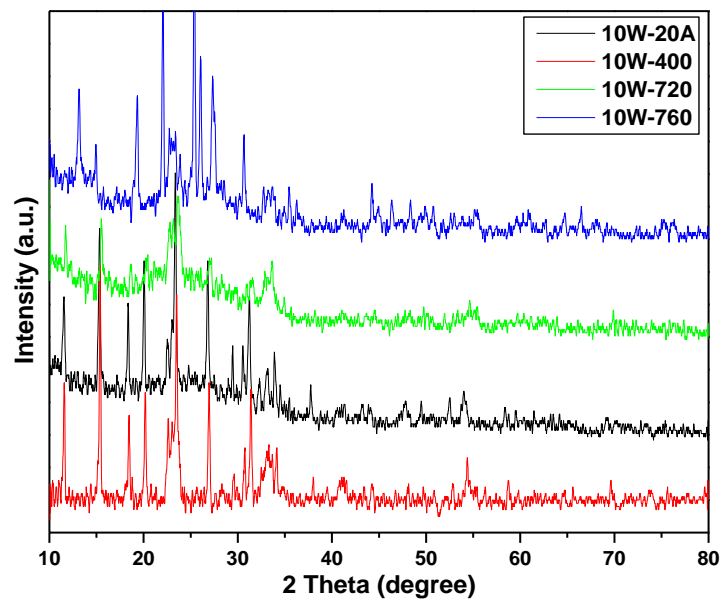


Figure 1b. X-ray diffraction profiles of 10 wt.% WO_3 supported on Y- zeolites and mordenite with different Si/Al ratios.

FT-IR analysis

Figures 2a and 2b represent the FT-IR spectra of different WO₃ loadings supported on Y-zeolite and 10 wt.% WO₃ over different zeolites (Y and mordenite), respectively. A representative FT-IR spectrum of synthesized WO₃/Y-zeolite catalysts shown a broadband spectrum between 3000 to 3700 cm⁻¹, which corresponds to the isolated Si-OH, Al-OH and O-H groups with stretching vibration modes (asymmetric and symmetric) and O-H bending vibrations at 1630 cm⁻¹ associated with coordinated water molecules (Figure 2a and Figure 2b). Bands at 1010, 1200, 836 and 459 cm⁻¹ were assigned to bonding Si-O-Si and Si-O-Al primary structural units, and the bands at 611 and 529 cm⁻¹ were assigned to SiO₄ and AlO₄ pseudo-lattice tetrahedral structures of zeolite framework. An additional peak was observed at 775 cm⁻¹ in all the impregnated samples, which attributes to the W-O-W vibrational modes of two connecting WO₆ species [26].

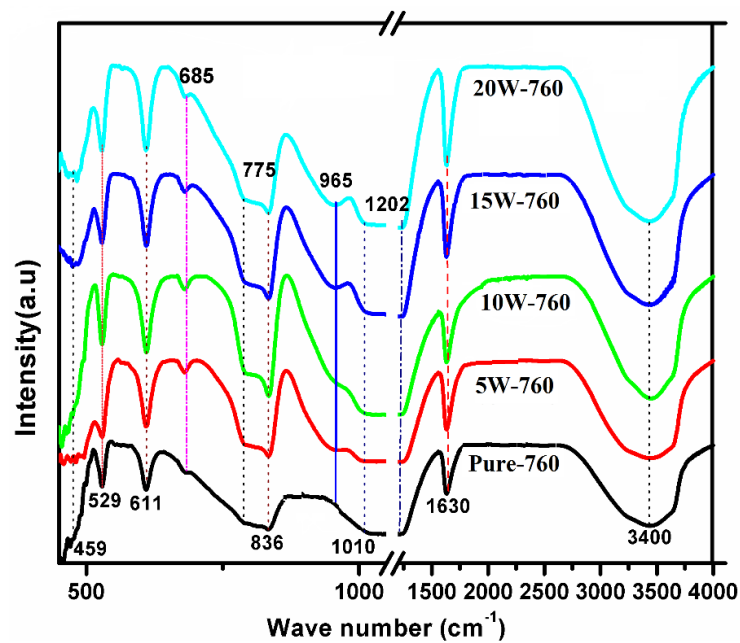


Figure 2a. FT-IR profiles of different WO_3 loadings (0-20 wt.%) supported on Y-zeolite(CBV-760).

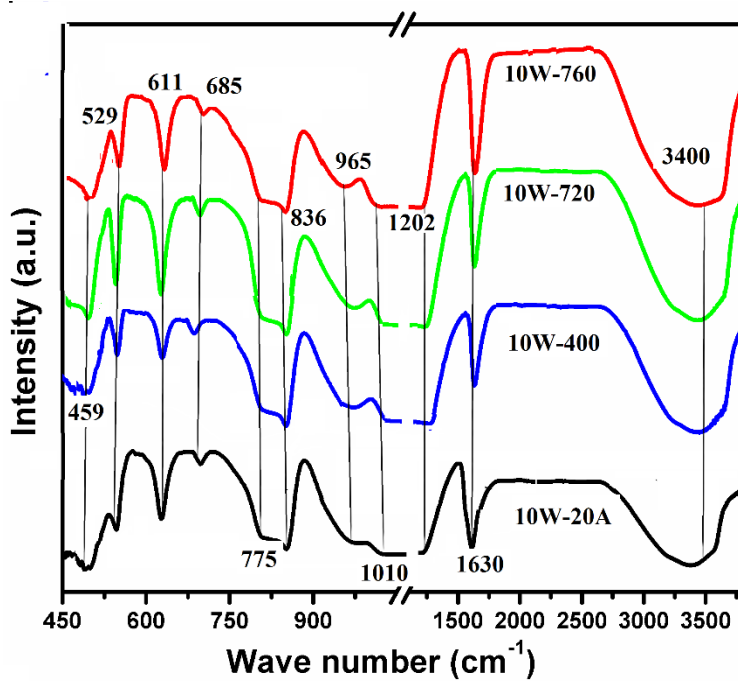


Figure 2b. FT-IR profiles of 10 wt.% WO_3 supported on different Y- zeolites (Si/Al ratios) and mordenite.

N₂ physisorption results

Table 1 provides the results of textural features of all the prepared samples with different Si/Al ratios. It was clearly visible that surface area and pore volume decreased with WO₃ loadings (5-20 wt.%) [27]. It confirms the incorporation of the active phase (WO_x) presented partially inside the micropores of zeolite structure. Fig. 3a & 3b represents the nitrogen adsorption-desorption isotherms for different WO₃ loadings supported on Y-zeolite and, 10 wt.% WO₃ supported on different zeolites, respectively. According to the IUPAC classification, the isotherms curve has a well-defined plateau and can be classed as a Type-I hysteresis loop defining a highly microporous character. At low relative pressures (0.1), primary adsorption occurs, indicating the creation of micropores with a narrow and restricted pore size distribution. The accessible micropore volume with a limiting absorption capacity is due to interior bulk pore steric hindrance [28]. In addition, a smaller mesopores network was analysed by the hysteresis isotherms by capillary condensation.

Table 1. Physico-chemical characteristic properties of various loadings of WO₃ supported on Y-zeolites.

Catalyst code	Si/Al ratio	BET Surface area (m ² /g)	Average Pore diameter (nm)	Total Pore Volume (cc/g)
Pure-760	60	552	2.47	0.33
5W-760	60	527	2.46	0.32
10W-760	60	477	2.37	0.29
15W-760	60	386	1.84	0.24
20W-760	60	327	1.2	0.20
10W-20A	20	375	2.2	0.21
10W-400	5.1	534	2.14	0.29
10W-720	30	511	2.51	0.32
10W-760	60	477	2.37	0.29

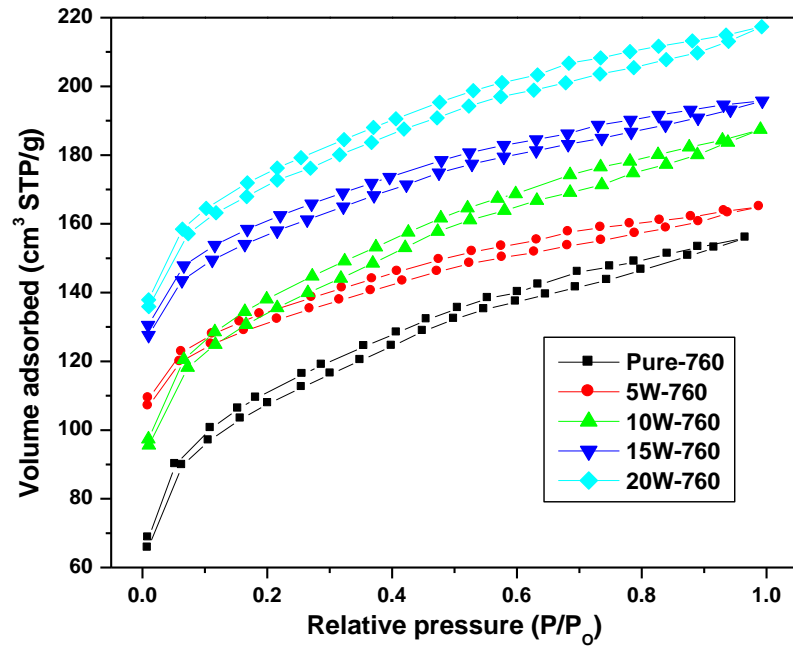


Figure 3a. N₂- adsorption desorption isotherms of different weights of WO₃ supported on Y-zeolite(CBV-760)

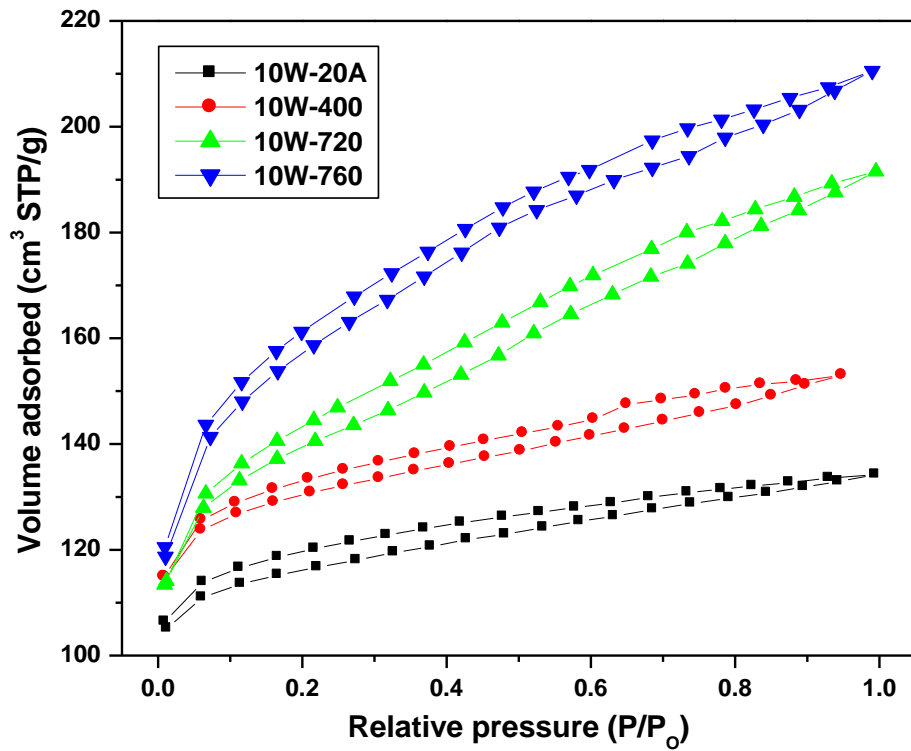


Figure 3b. N₂ adsorption-desorption isotherms over 10 wt.% WO₃ supported Y and mordenite zeolites with different Si/Al₂O₃ ratios.

Temperature programmed desorption

The total surface acidity of WO₃ modified zeolites was determined by NH₃-TPD analysis and the ammonia desorption curves are shown in Figs. 4a and 4b. The total acidity and their respective acid site strength distribution of different samples were measured by desorption of ammonia profiles were observed between 100°C to 700 °C (Table 2).

The quantification of total acidity is an important surface property that determines the reactivity during the esterification reaction (Table 2). The total acidity increased with WO₃ loadings over zeolites supported catalysts from 5 wt.% to 20 wt.% WO₃ compared to pure Y-zeolite. The TPD evaluation indicates that the amount of acidity and the strength of the acid sites increased with the incorporation of WO₃ component to the Y-zeolite support. Furthermore, the acidity strength of zeolite surface was significantly altered by adding WO₃. Typically, three common types of acidity strength i.e., weak, moderate, and strong acid sites strength are exhibited by the NH₃ desorption profiles at elevated temperatures by the metal-modified zeolites. After wet impregnation of tungsten oxide species over zeolite surface enhances the weak and moderate acid sites density. The absence of strong acid sites was found over zeolite-supported catalysts, and it indicates that the original acid sites of the Y-zeolite were partially blocked at low WO₃ loadings (below 15 wt.%). In addition, at higher loadings i.e., for 15 and 20 wt.% WO₃-720 catalysts exhibited strong acid sites at high temperatures; this might be due to the oligomeric WO_x species and this phenomenon was also supported by the XRD analysis [29].

Figure 4b represents the NH₃-TPD profile of 10 wt.% WO₃ supported Y and mordenite zeolites. The total acidity and strength vary with the Si/Al ratio, which significantly influence the reaction performance. The SiO₂/Al₂O₃ ratios for Y zeolites are denoted as CBV-400, CBV-720, CBV-760 and CBV-20A are 5.1, 30, 60, and 20

respectively. From Fig. 4b one can clearly observe that 10W-CBV 400 possesses a greater amount of total acidity than the other zeolites. The total amount of acidity values given after integrating the individual peaks which are presented in Table 2. As predicted, the CBV-400 with the lowest SiO₂/Al₂O₃ ratio exhibited the highest total acidity in this work. The acidity is relatively higher at low Si/Al ratios content in zeolites.

Table 2. Total amount of acidity of various loadings of WO₃ supported on different Y-zeolites calculated from NH₃-TPD analysis.

Catalyst code	Peak I	Peak II	Peak III	Total acidity (cc/g)	Acid site density ^a (mmol/m ²)
Pure-760	1.98	0.49	2.15	4.62	0.083
5W-760	2.99	1.99	1.38	6.08	0.011
10W-760	3.45	2.62	1.55	7.62	0.016
15W-760	5.63	2.37	2.18	10.18	0.026
20W-760	6.68	3.84	2.32	12.84	0.039
10W-20A	16.19	0.21	2.03	18.43	0.049
10W-400	25.9	---	1.43	27.33	0.051
10W-720	9.46	---	1.50	12.84	0.025
10W-760	3.45	2.62	1.55	7.62	0.016

a-Total acidity/Surface area

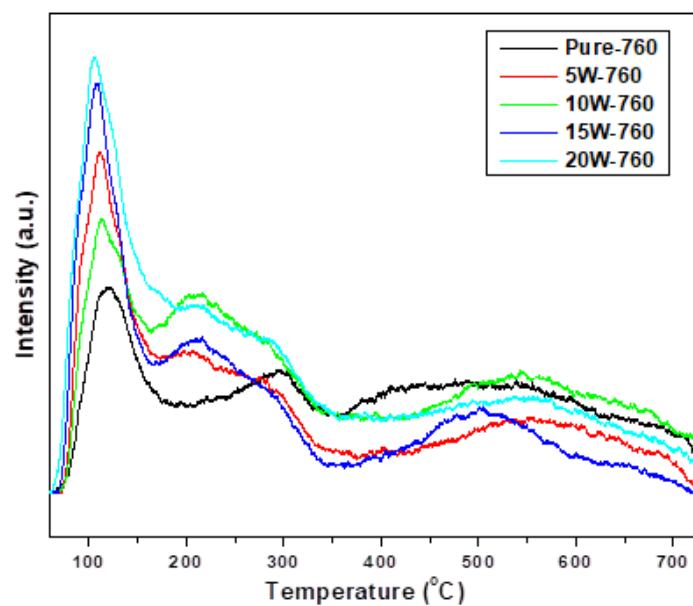


Figure 4a. NH₃-TPD profiles of various loadings of WO₃ supported on Y-zeolite (CBV-760).

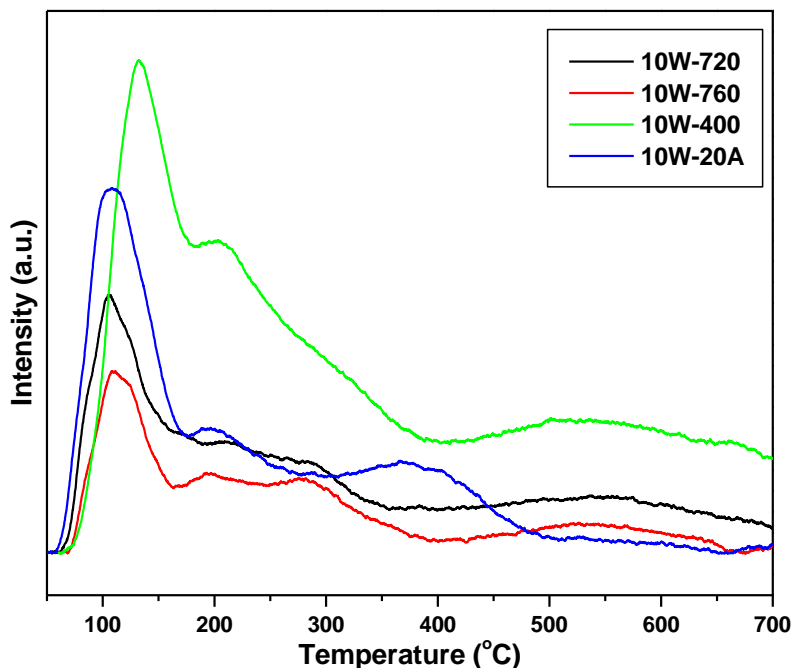


Figure 4b. NH₃-TPD profiles of 10 wt.% WO₃ catalysts supported on Y- zeolites with different Si/Al₂O₃ ratios.

Catalytic activity

The catalyst activity tests were studied in a fixed bed reactor operating at atmospheric pressure. Initial testing has been carried out to evaluate the effect of catalyst-support correlation in the esterification of lactic acid reaction activity (Figure 5). The desired product formed in the lactic acid esterification with butanol is the butyl lactate, along with by-products formation was initiated by secondary reactions of butyl lactate further to produce ethers of butyl lactate with unreacted butanol. Moreover, the by-products, including o-butoxy lactic acid and o-butoxy n-butyl lactate formation, were evident from the dehydration of lactic acid and n-butyl lactate with butanol respectively (Scheme 1). However, the di-butyl ether was found to be one of the major products in the

analysis. However, the selectivities were not considered since the di-butyl ether comes from the dehydration of two butanol molecules, which is an excess reactant and/or used as a solvent during esterification. The conversion of alcohols was found to be the highest for 10W-760 and followed in the descending order: 10W-760>10W-720>10W-400>10W-20A. This implies that the difference in their conversion levels can be attributed to the difference in total acidity of zeolites and the selectivity also followed a similar trend. Whereas 10W-20A exhibited higher acidity than 10W-760 and 10W-720 catalysts. Thus, it forms the ester with the lowest selectivity. This might be due to the strong acidic sites observed in TPD analysis for 10W-20A that favor other side reactions with larger amounts of by-products. The activity of the reaction strongly depends on the acidity strength, moreover, weak, and moderate acid sites are important and favors the desired reaction rate and selectivity of the product. This also suggests that the catalyst with optimal acidity strength with greater amount of acid sites will gain the best performance in terms of conversion and lactate selectivity. Thus, the 10W-760 catalyst exhibited the highest butyl lactate selectivity ~ 81%, with 87% lactic acid conversion.

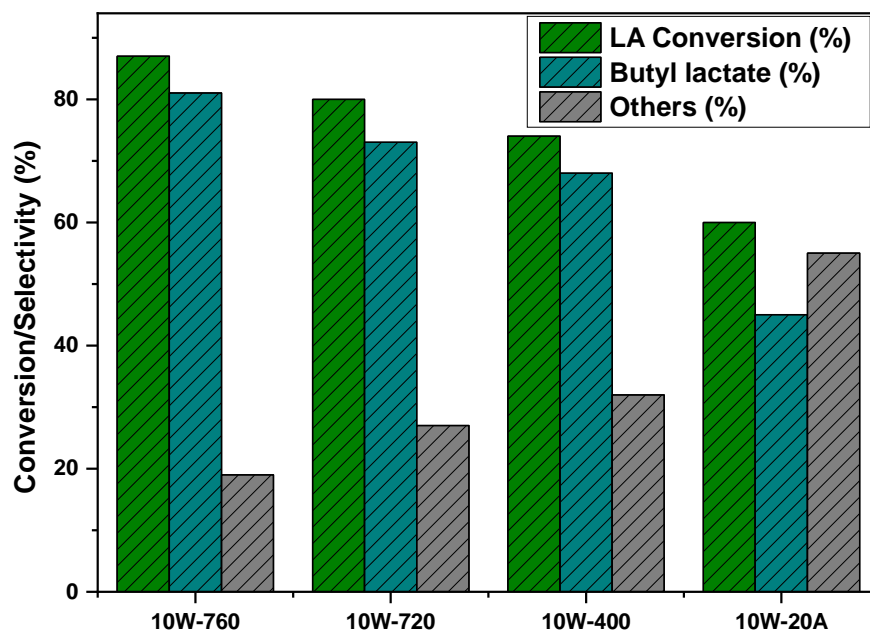
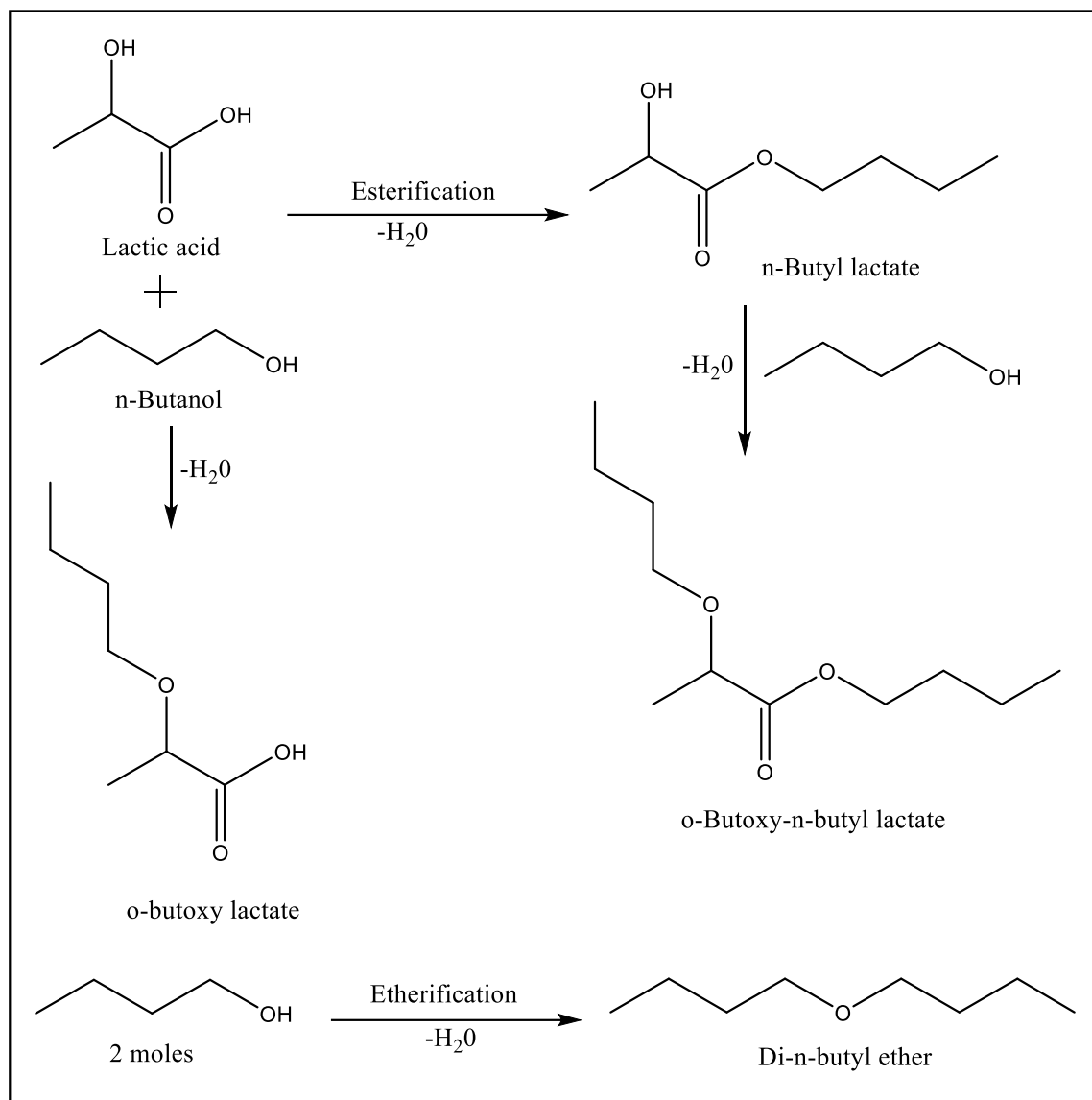


Figure 5. Effect of Si/Al ratios in Y-zeolites and mordenite supported for 10 wt.% WO_3 . **Reaction conditions:** LA:BtOH mole ratio = 1:3, feed flow = 1.0 mL/h, carrier gas (N_2) = 30 mL/min, reaction temperature = 175°C, and catalyst amount = 300mg, others = o-butoxy lactic acid and o-butoxy n-butyl lactate.



Scheme 1. The proposed reaction pathways of lactic acid esterification with n-butanol over Y-zeolite catalyst.

Effect of WO_3 loadings

The effect of loadings of WO_3 on Y-zeolite (CBV-760) was investigated and varying WO_3 had a profound influence on exhibiting different catalytic activities on lactic acid esterification. As predicted, in the absence of a catalyst, the esterification presented low activity and selectivity. Over 10 wt.% WO_3 (10W-760) catalyst displayed the highest lactic acid conversion and butyl lactate selectivity. Further, the conversion increased with

WO₃ loadings; nevertheless, activity declined thereafter 10 wt.% WO₃ content. The conversion and selectivity reached a maximum at an optimal level of 10 wt.% WO₃. The 10 wt.% WO₃ catalyst possesses weak and moderate acid sites in higher amounts than other catalysts. Herein, the selective reaction mechanism follows profoundly with the highest total acidity, which plays a vital role in esterifying the lactic acid in the desired pathway. However, 15 and 20 wt.% WO₃ CBV-760 catalysts exhibited the highest total acidity, but their selectivity towards butyl lactate declined due to strong acid sites, which promotes the secondary reactions to form by-products. At higher WO₃ loadings (above 10 wt.%), we found that the WO₃ covers and blocks the most of the relevant weak and moderate acid sites, and further, the agglomeration of WO₃ has occurred. From TPD-NH₃ analysis, the number of strong acid sites increased with loadings above 10 wt.%, *i.e.*, for 15 & 20 wt.% WO₃ in CBV760 catalyst. The strong acid sites participate more in the side-reactions mechanism in by-products formation than weak and moderate acid sites. The activity results are well correlated with the total acidity and strength of acidity of the zeolite-based catalysts. The catalyst activity results are well supported by the XRD and TPD analysis. Henceforth, the active and selective CBV760 catalyst was chosen to determine the most optimized reaction conditions, such as reaction temperature, LA to alcohol mole ratio and the effect of alcohol.

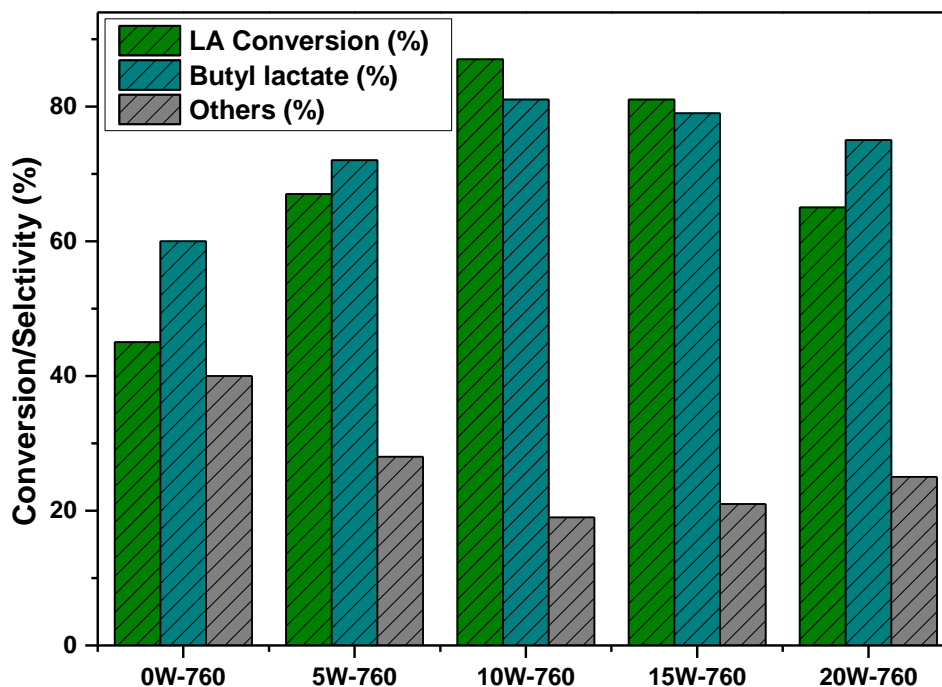


Figure 6. Effect of various WO₃ loadings (0-20 wt.%) supported on Y-zeolite (CBV-760) catalysts. **Reaction conditions:** LA:BuOH mole ratio = 1:3, feed flow = 1.0 mL/h, carrier gas (N₂) = 30 mL/min, reaction temperature = 175°C, and catalyst amount = 300mg, others = o-butoxy lactic acid and o-butoxy n-butyl lactate.

Effect of reaction temperature

Figure 7 shows the reaction temperature effect on the LA conversion and butyl lactate selectivity over 10W-760 catalyst in the temperature range of 175 – 250 °C while keeping the acid-alcohol concentration at 1:3. Maximum esterification of lactic acid was observed at lower reaction temperatures. While increasing to higher temperatures above 200 °C the conversion of lactic acid was observed at a maximum of about 80%, but the selectivity towards esterification reaction was decreased due to the formation of by-products. However, by lowering the temperature to less than 170 °C, the lactic acid feed was not fully vaporized in combination with the butanol to proceed with the esterification reaction. Thus, we observed that 175 °C is the optimized reaction temperature for lactic acid esterification with butanol.

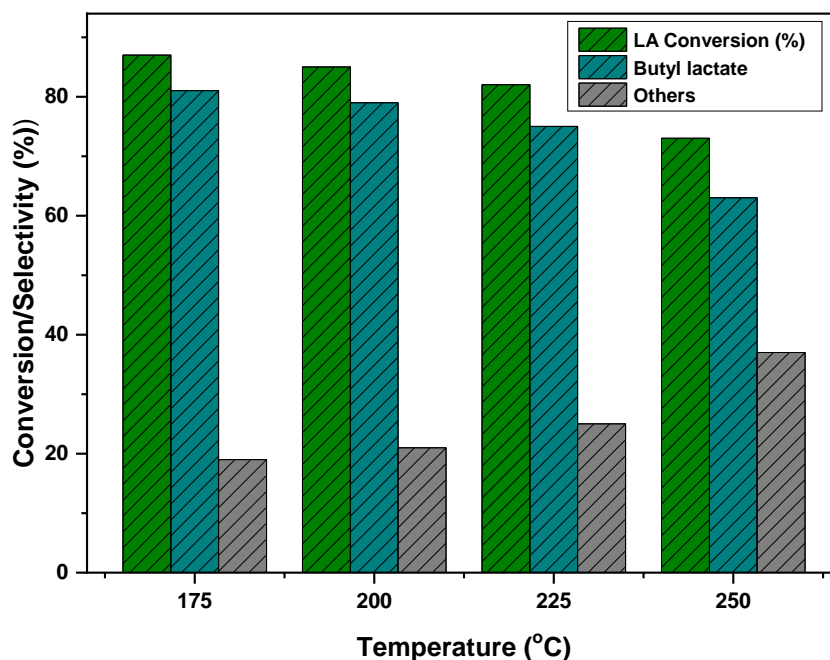


Figure 7. Effect of reaction temperature for lactic acid esterification over 10 wt.% WO_3 supported on Y-zeolite (CBV-760). **Reaction conditions:** LA:BtOH mole ratio = 1:3, feed flow = 1.0 mL/h, carrier gas (N_2) = 30 mL/min, and catalyst amount (10W-760) = 300 mg, others = o-butoxy lactic acid and o-butoxy n-butyl lactate

Effect of LA to BtOH mole ratio

The reaction was carried out over 10W-760 catalyst using different molar ratios of lactic acid to butanol and the results were presented in Figure 8. Initially, the conversion of Lactic acid increased with the concentration of butyl alcohol in the reaction mixture 1:1 to 1:3 rations i.e., lactic acid:butylalcohol). In the case of 1:1 lactic acid to butanol mole ratio, the conversion of Lactic acid was observed as less than that of 1:3 LA to butanol ratio. This is because, at lower butanol concentrations, their availability is fairly less to react with the lactic acid for dehydration. While in the case of 1:5 and 1:7 LA to butanol ratio, the conversion towards esterification was decreased relative to that of 1:3 and 1:1 mole ratio. This might be due to the greater number of butanol molecules that were adsorbed per m^2 with the active sites of the catalyst surface, which leads to the formation

of dibutyl ether. This is an important reason why the catalysts with a high amount of acidic site show a lower conversion rate of lactic acid. The alcohol is easily adsorbed on the site show a lower conversion rate of lactic acid. The alcohol is easily adsorbed on the highly available acid sites, resulting in an unwanted self-etherification reaction. Thus, from all the above observations, one can conclude that 1:3 lactic acid-butanol mole ratio offers better catalytic activity in terms of LA conversion (87%) and butyl lactate selectivity (81%).

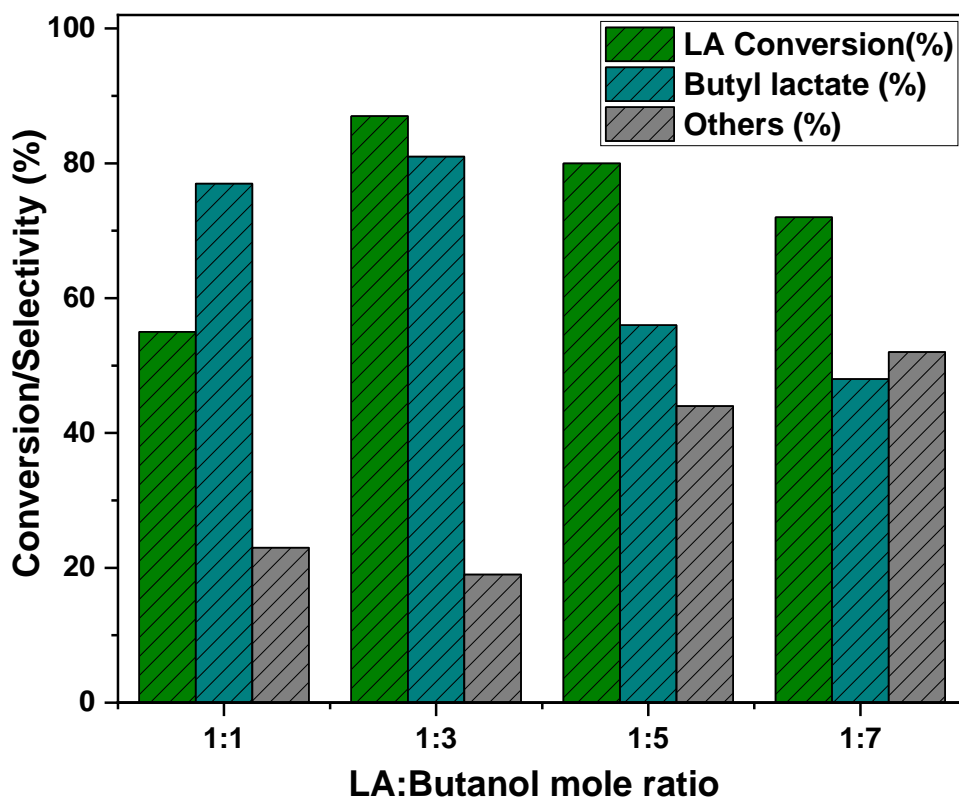


Figure 8. Esterification of lactic acid with butanol at different LA: BtOH mole ratios over 10 wt.% WO₃ supported on Y-zeolite (CBV-760). **Reaction conditions:** feed flow = 1.0 mL/h, carrier gas (N₂) = 30 mL/min, reaction temperature = 175 °C and catalyst amount (10W-760) = 300mg, others = o-butoxy lactic acid and o-butoxy n-butyl lactate.

Esterification of lactic acid with different alcohols

The esterification of lactic acid with different alcohols has been investigated in the optimized reaction conditions. The active 10wt.% WO_3 -CBV-760 catalyst, exhibited a slightly bit higher conversion over methanol reactant than other alcohols. The descending order of conversion follows: methanol > ethanol > propyl alcohol > butyl alcohol. In case butyl and propyl alcohols reactants delivered similar results in terms of conversion and selectivity. However, the lactate selectivity is slightly higher in the case of butyl and propyl than in lower chain alcohols. From the results, it is evident that higher alcohols favor slightly better selectivity than lower-chain alcohols [30].

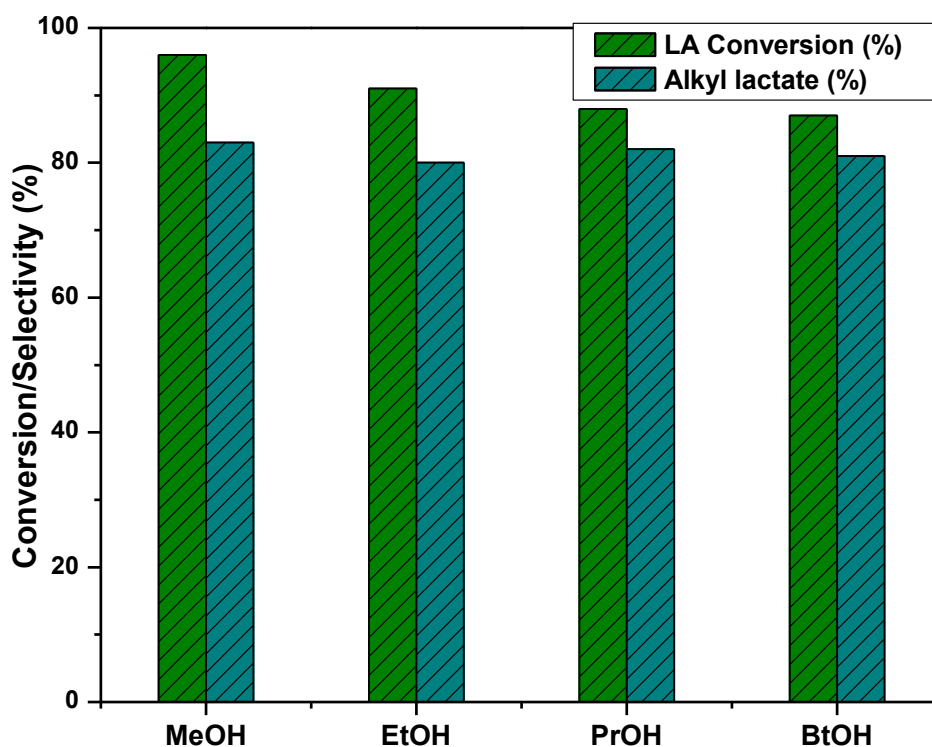


Figure 9. Esterification of lactic acid with different alcohols over 10 wt.% WO_3 supported Y-zeolite (CBV-760) catalyst. **Reaction conditions:** LA:alcohol mole ratio = 1:3, feed flow = 1.0 mL/h, carrier gas (N_2) = 30 mL/min, reaction temperature = 175 °C and catalyst amount (10W-760) = 300 mg.

Conclusions

Vapour phase esterification of lactic acid with butanol was carried out over tungsten oxide supported on zeolite catalysts. The effect of WO_3 loadings and the Si/Al ratio had profound effect on the catalyst performance. The acidity and acid sites density increased with WO_3 loadings. The degree of esterification depends on the acidity amount and strength of acid sites on the surface of the catalyst. Weak and moderate acid sites favor the selectivity of the butyl lactate and strong acid sites enhance the selectivity of the secondary reaction, which led to decrease in the selectivity of butyl lactate. The high amount of acid sites decreases both conversion and selectivity and promotes the self-etherification of butanol molecules and leads to the unavailability of alcohol molecules for the esterification reaction. The catalytic results suggest that the optimal 10 wt.% WO_3 supported Y-zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3=60$ catalyst achieved the highest lactic acid conversion and butyl lactate selectivity. Under the optimized reaction conditions (175 °C, 1:3 LA-BtOH feed flow rate=1.0 mL/h) the 10W-760 catalyst produces an overall yield of 70 % with 87% conversion and 81% selectivity towards butyl lactate.

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Y-zeolites modified with tungsten oxide catalyst for the esterification of lactic acid

Supplementary Information

Table.S1: Comparison of various catalysts reported in the literature

Type of reaction	Catalysts	Solvent	Reaction conditions	%Conversion / %yield	Reference
Liquid phase heterogeneous	tin(II) modified heteropolyacid $H_3PW_{12}O_{40}$ (HPW)	Methanol Ethanol Octanol	Amount of catalyst: 0.3 mol%, 900 rpm, 80 °C for 2 h Solvent ratio: 1:6	90.7 / 90.7 79.4 / 79.4 95.9 / 95.9	a
Liquid phase heterogeneous	TiO ₂ -ZrO ₂ (3:1)	n-Butanol	170°C, 200rpm, 1.32 g of lactic acid, 0.32 g of catalyst, 14 ml of n-butanol	94.2 % Yield	b
Liquid phase heterogeneous	TiO ₂ -Al ₂ O ₃ (1:1)	n-Butanol	140°C, 2.8 g of lactic acid, 0.64 g of catalyst, 30 ml of n-butanol	95.7 % Yield	c
Enzymatic esterification	Immobilized lipase B / Supercritical trifluoromethane	n-Butanol	55°C, 30Mpa, 26h	88.2% conversion	d
Batch reactive distillation	Cation exchange resin (amberlyst 15)	n-Butanol	30% LA (w/w), 5h, 45-96°C, catalyst loading (10-236 gms/mol of lactic acid,	92% conversion	e
Vapour phase heterogeneous (fixed bed reactor)	10W-760	n-Butanol	175 °C, 1:3 LA-BtOH, feed flow rate = 1.0 mL/h)	70% yield	This work