



Effective synthesis of cetyl palmitate over co-precipitated $\text{WO}_3\text{-ZrO}_2$ catalysts

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Abstract

This study is focused on the development of solid acid catalysts for the synthesis of long chain fatty acids. A series of $\text{WO}_3\text{-ZrO}_2$ catalysts were prepared by co-precipitation method and tested in the synthesis of cetyl palmitate. The effect of WO_3 loading (10, 15, and 20 wt% WO_3) and calcination temperature (700 and 800 °C) on the catalyst properties and activity was investigated. XRD and Raman analysis confirmed that WO_3 loading stabilized the tetragonal zirconia phase. Higher calcination temperature enhanced the acidities of the catalysts. $\text{WO}_3\text{-ZrO}_2$ catalysts were found to be very efficient for the synthesis of cetyl palmitate with high selectivity. These catalysts were tested for different reaction temperatures (135 and 162 °C), feed composition and catalyst amounts. The highest cetyl palmitate yield (98.4%) was obtained over the catalyst calcined at 800 °C with 15 wt% WO_3 , which had the highest total acidity. The catalysts preserved their activities up to three reuse.

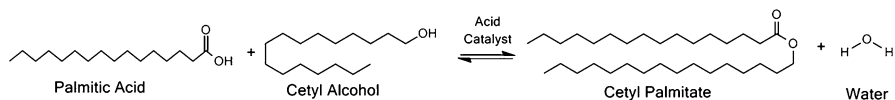
Keywords Cetyl palmitate · Esterification · Tungstate zirconia catalyst · Solid acid catalyst · Cetyl alcohol esterification · Palmitic acid

Introduction

Esters of long chain fatty alcohols and fatty acids are called wax esters. Wax esters have good lubricating properties along with biodegradability and no toxicity. They can be extracted from some limited natural sources such as seafowl feathers, jojoba seeds, honeycomb, carnauba, sheep wool and skin lipids. These esters are of industrial importance because they are used as emulsifiers and oiling agents in cosmetics, additives in lubricants, coating materials and plasticizers [1, 2]. Cetyl palmitate, the ester of cetyl alcohol and palmitic acid (Scheme 1), is one of the most

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Scheme 1 Cetyl alcohol esterification with palmitic acid

commonly used wax esters in cosmetics industry. It is the main constituent of spermaceti wax found in the skull of physeter catodon (a special whale kind) [3].

Since the natural sources of wax esters are limited, it is required to develop routes for producing them synthetically. Therefore, industrial production of esters are commonly performed by Fischer esterification with concentrated homogeneous acid catalysts, such as H_2SO_4 , HCl and H_3PO_4 . However, these catalysts have significant disadvantages that are corrosiveness, susceptibility to water, need for excess reagents, difficulties in product purification and environmental hazards [4, 5]. In order to overcome these problems, there are several studies in the literature about the development of active, selective and reusable heterogeneous catalysts. Though various catalysts such as acidic resins [6], zeolites [7], heteropoly acids [8] and sulfated zirconia incorporated mesoporous silicas [9] are studied, the success of the activity of these catalysts are limited to the esterification of carboxylic acids with short chain alcohols yielding esters with less than 10 carbons. There are a small number of studies about the esterification of long chain fatty acids and alcohols. Cirillo et al. studied the synthesis of cetyl palmitate by esterification the cetyl alcohol with palmitic acid in a solvent-free system using commercial lipase Lipozyme RM IM as catalyst and found promising results [10]. Mantri et al. investigated the use of various supported and unsupported multivalent salt hydrates for the esterification of long chain fatty acids and alcohols and found that ZrO^{2+} might be an active metal cation for the reaction [1]. However, the studies do not give a good understanding about the effects of catalyst properties on the ester yield due to the lack of detailed catalyst characterization results. Previously our group showed that the Zr-SBA-15 is an active and reusable catalyst for the synthesis of cetyl palmitate. Moreover, the activity of the catalyst for this reaction is strongly related to the acidity and the amount of Brønsted acid sites of the catalysts rather than the surface area [11].

Zirconia is a well-known support for catalysts and it has three stable crystalline phases: cubic, monoclinic and tetragonal. Doping zirconia with sulfates stabilized the tetragonal phase and creates additional electron deficient groups which may generate new acid sites and improves the Brønsted acidity [12]. Thus, sulfated zirconia has attracted much attention with its strong acidity and tested in many reaction including cracking, alkylation, isomerization and esterification [13, 14]. Nevertheless, the loss of sulfate during thermal treatments as well as the catalyst deactivation during the reaction due to the sulfate leaching, resulted in the interest for alternative oxoanions for sulfates [14]. Hino and Arata reported the preparation of a super solid acid catalyst by WO_3 impregnation over ZrO_2 as an alternative for sulfated zirconia [15]. Since then, $\text{WO}_3\text{-ZrO}_2$ catalysts were greatly investigated and found to be active, stable and promising catalysts for acid catalyzed reactions such as alkylation, etherification, isomerization, acetylation and oxidation

[12, 16–19]. Even though it is known that $\text{WO}_3\text{-ZrO}_2$ catalysts are less active compared to their sulfate promoted counterparts, they have significant advantages for industrial application, such as higher stability, easier regeneration and lower deactivation rates during catalysis [20]. The previous studies showed that the catalytic activity of $\text{WO}_3\text{-ZrO}_2$ catalysts may be attributed to the synergy between WO_3 and ZrO_2 . W loading and annealing temperature and preparation method are important factors for the creation of strong acid sites and stabilization of tetragonal ZrO_2 phase [19, 20]. The most common method for $\text{WO}_3\text{-ZrO}_2$ preparation is impregnation of zirconium hydroxide with an appropriate tungstate salt solution. However, Santiesteban et al. compared the tungstated zirconia catalysts prepared by both impregnation and co-precipitation methods having similar W loadings in *n*-pentane isomerization and stated that, the co-precipitated catalyst had twice the amount of strong acid sites and displayed higher activity. Co-precipitation method yields in better dispersion of WO_x species, higher acidity and higher surface area than those of impregnation [19].

Although $\text{WO}_3\text{-ZrO}_2$ catalyst have been extensively investigated for different acid catalyzed reactions, to the best of our knowledge, their activity in the esterification of long chain carboxylic acids and fatty alcohols to synthesize valuable fine chemical such as cetyl palmitate has not been studied yet. Here, we report the effect of W loading and calcination temperature on the properties of co-precipitated $\text{WO}_3\text{-ZrO}_2$ catalysts and their activity in the synthesis of cetyl palmitate. The influence of reaction parameters such as temperature, catalyst amount and feed composition and the reusability of the active catalysts were also studied.

Experimental section

Preparation of Co-precipitated $\text{WO}_3\text{-ZrO}_2$ catalysts

The co-precipitated $\text{WO}_3\text{-ZrO}_2$ catalysts were prepared according to the procedure given by Zhang et al. [21]. Aqueous solutions of pre-determined concentrations of ammonium metatungstate hydrate and zirconium (IV) oxychloride were prepared and mixed in a 200 ml round bottom flask which was equipped with a reflux condenser. The mixed solution was heated to reflux for 2 h under vigorous stirring and then cooled down to room temperature. To perform the co-precipitation, the pH of resulting solution was adjusted to 9.5 by adding ammonium hydroxide solution dropwise with magnetic agitation. The obtained jelly precipitate was aged at room temperature for 24 h. Afterwards, the aged precipitate was centrifuged and washed with excess amount of deionized water to remove the chlorides. The product was dried at 110 °C overnight and calcined at 700 °C and 800 °C for 3 h. Three different WO_3 contents were investigated, 10 wt%, 15 wt% and 20 wt%. The prepared catalysts were named as WZ-XY, where X refers to the WO_3 wt% (10, 15 or 20) and Y refers to the calcination temperature (Y = 7 for 700 °C and Y = 8 for 800 °C).

Catalyst characterization

The BET surface area and pore size properties of the catalysts were determined by N₂ adsorption using Micromeritics ASAP 2010 model static volumetric adsorption instrument at 77 K on samples degassed at 200 °C for 2 h.

X-ray diffraction and Raman analysis were applied for the determination of structural properties. XRD analysis was performed by Philips X'Pert diffractometer with Cu K_α radiation. Raman spectra of the catalysts were acquired with an Argon laser at the excitation wavelength of 488 nm. The resolution was 4 cm⁻¹.

Temperature-programmed desorption of ammonia (NH₃-TPD) method was carried out to determine the acidity and acid site distribution of the catalysts using Micromeritics AutoChem II Chemisorption Analyzer instrument. The sample was heated up to 400 °C with a heating rate of 5 °C/min and kept at this temperature for 30 min under He gas flow of 70 ml/min. Then, the temperature was decreased to 60 °C at a rate of 5 °C/min under He flow of 30 ml/min. After the sample was subjected to NH₃-He flow at a rate of 30 ml/min for 30 min, it was degassed at 60 °C under He flow of 70 ml/min for 2 h to remove the physically adsorbed NH₃. TCD signal was recorded as the sample was heated to 700 °C with a heating rate of 10 °C/min.

Pyridine adsorption FTIR spectroscopy method was used to determine the Brønsted and Lewis acidity characteristics of the catalysts. For a typical analysis, the sample was activated at 300 °C under vacuum (2×10^{-2} mmHg) for 2 h followed by the adsorption of pyridine was carried out at 120 °C for 30 min. Then, the sample was kept 120 °C under N₂ flow of 30 ml/min for 2 h to remove the physisorbed pyridine. IR spectra were obtained by Shimadzu FTIR 8400S model Fourier Transformed Infrared Spectrometer between 400 and 4000 cm⁻¹ using 3 wt % sample pellets prepared with KBr.

The elemental analysis was performed by XRF analysis with powder method using Spectro IQ II instrument and Cu K_α radiation.

Catalytic activity

The esterification of cetyl alcohol (CA) (Fluka 52238) and palmitic acid (PA) (Sigma P0500) were carried out under N₂ atmosphere in a 100 ml round bottom flask equipped with a Teflon coated magnetic stirring bar with a stirring rate of 1000 rpm and a reflux condenser. For a typical reaction, 100 mg catalyst was added into 15 ml of mesitylene and heated up to 162 °C followed by the addition of an equimolar solution (3.75 mmol) of CA and PA in 10 ml of mesitylene. Reaction samples taken at regular intervals were analyzed by Agilent 6890 gas chromatograph using Ultra 1 (25 m × 0.3 mm) capillary column equipped with FID. The injector and detector temperatures were 280 °C and 320 °C, respectively. The oven temperature was increased from 50 to 300 °C at a rate of 12 °C/min and it was kept at 300 °C for 35 min. The carrier gas was Helium with a flow rate of 37.3 mL/min. The split ratio was 24.9:1. The conversion of cetyl alcohol (CA) and yield of cetyl palmitate (CP) were calculated using the Eqs. 1 and 2 respectively.

$$\text{Conversion}(\%) = \frac{(CA_{in} - CA_{out})}{CA_{in}} \times 100 \quad (1)$$

$$\text{Yield}(\%) = \frac{CP_{out}}{CA_{in}} \times 100 \quad (2)$$

The three catalysts which gave the highest ester yields were tested to determine their reusabilities. For this, the used catalysts were recovered by filtration and washed twice with mesitylene and methanol. After drying overnight at 110 °C, they were tested in the esterification reaction.

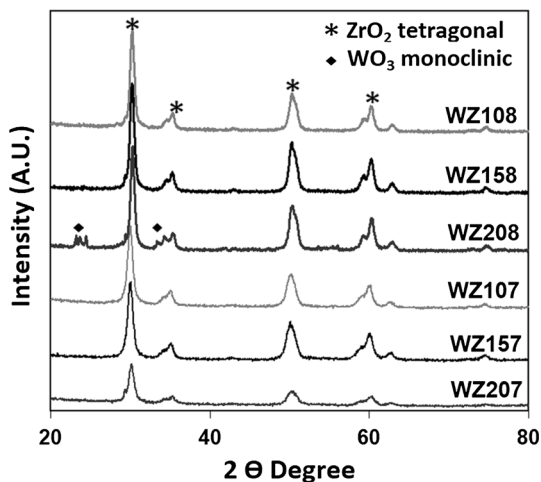
Results and discussion

Catalyst characterization

Phase characterization and surface properties

The effect of WO_3 loading and calcination temperature on the crystal structure of the $\text{WO}_3\text{-ZrO}_2$ catalysts might be observed from the XRD patterns of the catalysts given in Fig. 1. All the co-precipitated $\text{WO}_3\text{-ZrO}_2$ catalysts had characteristic peaks related to tetragonal zirconia. The intensities of these characteristic peaks increased with calcination temperature. Thus, it can be concluded that, high calcination temperatures stabilize the tetragonal zirconia phase. When the $\text{WO}_3\text{-ZrO}_2$ catalysts calcined at 800 °C with different WO_3 loadings compared, WO_3 loading increased the stability of tetragonal zirconia phase. There are no peaks related to the monoclinic WO_3 phases observed on the X-ray diffractograms of the catalysts except for WZ208. This might be caused by the well dispersion of WO_3 species for 10 and 15 wt% WO_3 loadings.

Fig. 1 XRD patterns of the catalysts prepared



Raman spectroscopy was applied as an additional method to explore the structures of the co-precipitated $\text{WO}_3\text{-ZrO}_2$ catalysts more sensitively (Fig. 2). All samples display the characteristic bands of tetragonal zirconia at 279, 320, 461 and 645 cm^{-1} [16, 20, 22, 23]. The bands observed at 601 cm^{-1} is attributed to W-O-Zr species which results from the interaction between tetragonal ZrO_2 and WO_3 . These species are responsible for the formation of strong acid centers. Furthermore, all catalysts except WZ108 show a broad band at 830 cm^{-1} assigned to W-O-W vibrations indicating the interactions between tungsten oxide groups and the presence of two-dimensional polytungstate clusters. The existence of these clusters might be responsible from the formation of strong Brønsted acid centers [20]. Increasing the calcination temperature leads to a decrease in the peak intensities at 601 and 830 cm^{-1} , which might be caused by the improved dispersion of tungsten oxide species at higher temperatures.

The surface areas and pore diameters of the catalysts are given in Table 1. The surface area of the co-precipitated $\text{WO}_3\text{-ZrO}_2$ catalysts decreased with higher WO_3 loading and calcination temperature. However, the pore diameters of the $\text{WO}_3\text{-ZrO}_2$ catalysts with 15 wt% loadings were higher than those with 10 wt% loadings. This might be explained by the stabilizing effect of the WO_3 on tetragonal ZrO_2 . As the WO_3 loading increased from 15 wt% to 20 wt% the pore diameter decreased due to the blocking of pores by WO_3 species.

Acidic properties

Total acidities and the acid strength of the catalysts were analyzed by $\text{NH}_3\text{-TPD}$ method and the resulting profiles are given in Fig. 3 and the values in Table 1. $\text{WO}_3\text{-ZrO}_2$ catalysts had considerably high total acidity and they all showed a broad acidity peak between 150 and $650\text{ }^\circ\text{C}$ indicating the presence of weak, moderate and also strong acid sites. When the effect of calcination temperature was considered by comparing the catalysts having the same WO_3 loadings, the high calcination temperature had an improving effect on the total acidity of the catalysts. This can be

Fig. 2 Raman spectra of the catalysts prepared

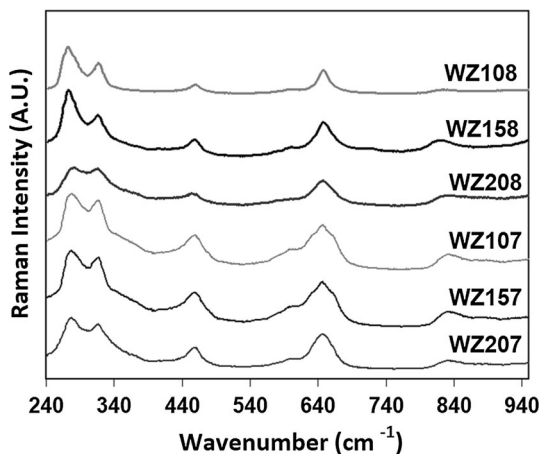
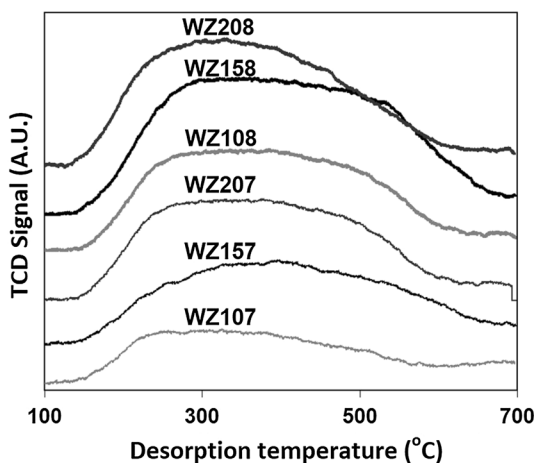


Table 1 Textural properties and total acidities of the catalysts prepared

Catalysts	BJH d_p (Å)	S_{BET} (m ² /g)	Acidity (mmol NH ₃ /g catalyst)	B/L ^a	Zr content (wt%)	W content (wt%)
WZ107	43.0	64.6	1.059	1.54	46.6	8.48
WZ157	56.1	57.1	1.669	1.98	46.9	12.1
WZ207	40.5	54.7	1.913	1.27	41.1	16.7
WZ108	56.9	51.6	1.932	1.61	48.3	8.43
WZ158	65.1	48.5	2.781	1.41	47.1	11.9
WZ208	52.2	48.3	2.263	0.75	46.6	16.2

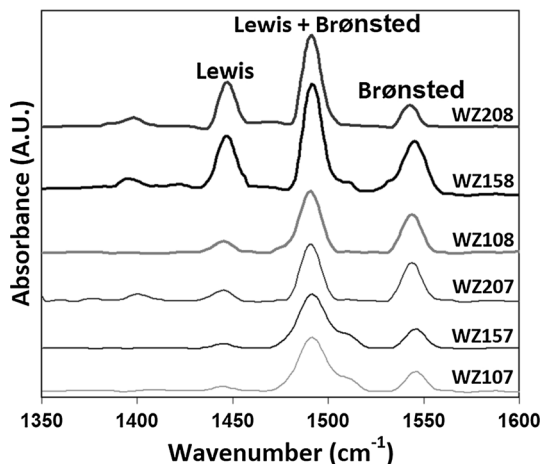
^aB/L defined as the ratio of the areas under the peaks at 1540–1445 cm⁻¹

Fig. 3 NH₃-TPD of the catalysts prepared

related with the stabilized tetragonal zirconia phase observed in XRD and Raman results. For the WO₃-ZrO₂ catalysts calcined at 700 °C, the total acidity increased with the WO₃ loading. Though, the highest total acidity obtained for the WZ158 (2.781 mmol NH₃/g catalyst). As the WO₃ loading increased to 20 wt%, the total acidity of the catalyst decreased. This might be caused by the presence of monoclinic WO₃ species, which were also detected by XRD analysis.

Another important property of the acidic catalyst is the acid site character. Depending on the reaction mechanism either Brønsted or Lewis acid sites might be effective. FT-IR spectra of the pyridine adsorbed catalysts are given in Fig. 4. There are three characteristic peaks in the spectra. Pyridinium ion bonding to the Brønsted acid site are indicated by the peaks at 1540 cm⁻¹, whereas the peaks at 1445 cm⁻¹ are related to the pyridine coordination on the Lewis acid sites and peaks at 1495 cm⁻¹ are assigned to both Brønsted and Lewis acid sites. The areas under the bands at 1445 cm⁻¹ and 1540 cm⁻¹ were related to Lewis and Brønsted acid site concentrations respectively to compare the concentrations of Lewis and Brønsted acid sites of the catalysts [24]. The Brønsted acid site/Lewis acid site ratio (B/L)

Fig. 4 FTIR spectra of pyridine adsorbed catalysts



was calculated by dividing peak area at 1540–1445 cm^{-1} and reported in Table 1. B/L ratio was affected by tungsten loading and calcination temperature. It changed between 1.98 and 0.75. Higher B/L ratio was obtained for lower tungsten loading and calcination temperature. WZ157 had the highest B/L while WZ208 had the lowest B/L ratio.

Synthesis of cetyl palmitate

Cetyl palmitate selectivities were higher than 98% over all the catalysts resulting in the formation of cetyl palmitate with high yields as the only major product.

Effect of WO_3 loading and calcination temperature

The results of the reaction tests over different catalysts are given in Fig. 5. The lowest cetyl alcohol conversion was obtained over WZ107 catalyst that also had the lowest acidity. All the other catalysts gave cetyl alcohol conversions about 90% which proved that $\text{WO}_3\text{-ZrO}_2$ were significantly active and promising catalysts for the synthesis of long chain fatty acid esters. It can be observed that higher cetyl alcohol conversions were obtained over the catalysts calcined at 800 °C. Those catalysts also had higher total acidities compared to the catalysts calcined at 700 °C regardless of the WO_3 content.

The activities of the catalysts were determined by initial disappearance rate of cetyl alcohol per gram of catalyst (r_0), which are given in Table 2. When the catalysts having the same amount of WO_3 calcined at different temperatures were compared, it was clearly observed that higher calcination temperature improved the activity of the catalyst and increased r_0 . The highest cetyl palmitate yield, 98.4%, was obtained over WZ158, which was the catalyst with the highest total acidity and a B/L ratio of 1.41. WZ208 catalyst having significant total acidity with B/L ratio of 0.75 also gave high ester yield, 92.9%. However, WZ107 catalyst having the lowest total acidity with a B/L ratio of 1.54 gave the lowest cetyl palmitate yield, 52.7%.

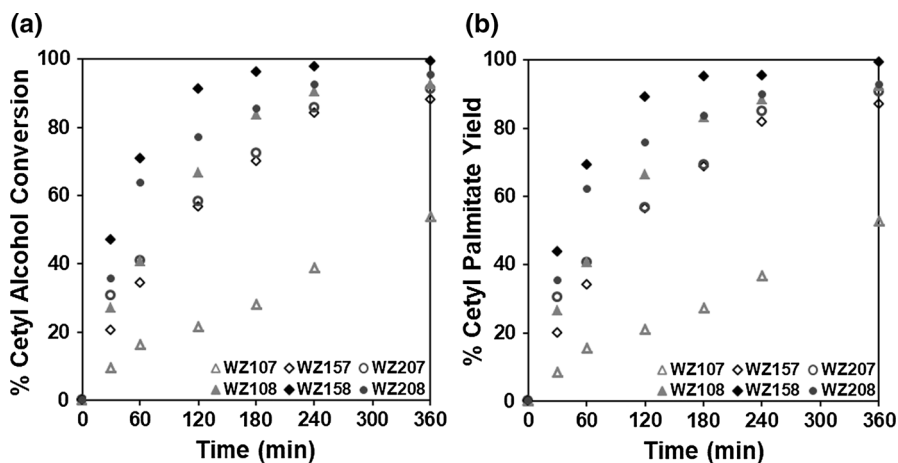


Fig. 5 **a** Conversion of cetyl alcohol and **b** yield of cetyl palmitate over the catalysts (reaction conditions: PA: CA mole ratio = 1:1, catalyst amount 5.32% (weight percent with respect to the total weight of reactants), solvent: mesitylene, stirring rate = 1000 rpm, N₂ atmosphere, reaction temperature = 162 °C)

Table 2 Initial rate of disappearance and conversion of cetyl alcohol and yield of cetyl palmitate over different catalysts (reaction conditions: PA: CA mole ratio = 1:1, catalyst amount 5.32% (weight percent with respect to the total weight of reactants), solvent: mesitylene, stirring rate = 1000 rpm, N₂ atmosphere, reaction temperature = 162 °C, 6 h reaction time)

Catalysts	$r_0 \times 10^5$ (mol/min g)	Conversion (%)	Yield (%)
WZ107	10.3	53.8	52.7
WZ157	21.5	88.3	87.3
WZ207	25.6	91.3	90.8
WZ108	25.5	92.7	92.4
WZ158	44.3	98.5	98.4
WZ208	40.0	95.5	92.9

These findings indicated that B/L ratio did not affect the activity observed, while total acidity was the determining factor for esterification reaction.

Reusability of the catalysts

The catalyst calcined at 800 °C were the three most active catalysts. They were tested to determine their reusabilities in esterification reaction and the results are listed in Table 3. All the catalysts showed good reusabilities without significant decrease in the cetyl palmitate yields after 3 cycles of reuse. WZ158 was the most active catalyst. It gave 95% cetyl palmitate yield even after the 3rd reuse.

Table 3 Initial rate of disappearance of cetyl alcohol and yield of cetyl palmitate over WZ108, WZ158 and WZ208 for three cycles of re-use (reaction conditions: PA: CA mole ratio = 1:1, catalyst amount 5.32% (weight percent with respect to the total weight of reactants), solvent: mesitylene, stirring rate = 1000 rpm, N₂ atmosphere, reaction temperature = 162 °C, 6 h reaction time)

Catalysts	1st use		2nd use		3rd use	
	$r_0 \times 10^5$ (mol/min g)	Yield of CP (%)	$r_0 \times 10^5$ (mol/min g)	Yield of CP (%)	$r_0 \times 10^5$ (mol/min g)	Yield of CP (%)
WZ108	25.5	92.4	22.1	90.8	21.9	87.4
WZ158	44.3	98.4	40.8	96.4	37.5	95.3
WZ208	40.0	92.9	35.6	91.5	33.5	90.4

Effect of reaction parameters

The reaction parameters such as the reaction temperature, catalyst amount and feed composition were studied in order to determine the optimum conditions for the reaction over WZ158. The resulting r_0 , cetyl alcohol conversion and cetyl palmitate yield values are given in Table 4 for all sets of experiments.

The effect of reaction temperature can be observed clearly when the entries 1 and 2 are compared. The increase in the reaction temperature significantly affected the initial rate of disappearance of cetyl alcohol and resulted in a higher cetyl palmitate yield, about 35% within the same reaction time when all the other parameters (catalyst amount and feed composition) kept unchanged. This was mainly attributed to the endothermic nature of the esterification reaction. Moreover, at 162 °C, which was the boiling point of mesitylene solvent, the water produced as a side product is also removed. Thus, the equilibrium of reaction shifted towards the product side.

When the catalyst amount reduced by half (entries 2 and 3), the initial rate of disappearance of cetyl alcohol dropped to almost one-third. Therefore, the cetyl palmitate yield decreased from 98.4 to 63.1% at the end of 6 h reaction time.

Since the esterification reaction is a reversible reaction, it is known that the yield can be increased by using one of the reactants in excess amount. However, it is important to be able to synthesize long chain fatty acid esters with high yields using

Table 4 Initial rate of disappearance of cetyl alcohol and yield of cetyl palmitate over WZ158 with different reaction conditions within 6 h of reaction time

Entry #	Temperature	CA/PA (mole)	Catalyst (%) ^a	$r_0 \times 10^5$ (mol/min g)	Conversion (%)	Yield (%)
1	135	1/1	5.32	6.73	64.3	63.1
2	162	1/1	5.32	44.3	98.5	98.4
3	162	1/1	2.66	16.0	69.2	63.1
4	162	1/2	5.32	54.2	98.9	98.6

^aWeight percent with respect to the total weight of reactants

equimolar amount of fatty alcohol and fatty acid in the reaction, because both fatty alcohols and acids are expensive reactants. When the results given in entries 2 and 4 were compared, it can be seen that using excess amount of palmitic acid increased the r_0 as expected. Nevertheless, the cetyl palmitate yield obtained at the end of the reaction was almost the same, indicating that the catalyst was good enough to synthesize high yields of long chain fatty esters with equimolar reactants.

Conclusions

Co-precipitated $\text{WO}_3\text{-ZrO}_2$ catalysts were very active, selective and reusable for the synthesis of cetyl palmitate. The characterization results showed that higher calcination temperature improved total acidity and Lewis acid sites notably. The total acidity was the determining factor for the activity of the catalyst in cetyl alcohol esterification with palmitic acid. B/L ratio did not affect activities observed. The highest yield, 98.4% was obtained over the most acidic catalyst, WZ158. The catalysts were re-usable without a significant decrease in their activities up to three cycles. The results were found to be very promising for the synthesis of long chain fatty acid esters with high yield.

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