

Experimental and Kinetic Studies of Esterification of Glycerol Using Combustion Synthesized $\text{SO}_4^{2-}/\text{CeO}_2\text{-Al}_2\text{O}_3$

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Abstract – An increase in the global production of biodiesel has resulted in the newfound significance of its byproduct, glycerol. The synthesis of acetins is an economical avenue to enhance the value of glycerol derived from biodiesel. WE developed an eco-friendly process for the synthesis of fuel additives from glycerol using a mixed oxide $\text{SO}_4^{2-}/\text{CeO}_2\text{-Al}_2\text{O}_3$ as catalyst. The $\text{CeO}_2\text{-Al}_2\text{O}_3$ mixed oxide was synthesized by the combustion method and then sulfated. The characterization of the catalyst was by means of XRD, BET, FTIR, and SEM. The influence of temperature, mole ratio and catalyst loading on the yield and selectivity of the acetins was studied for the esterification of glycerol. The reaction rate constants (k_1 , k_2 and k_3) were estimated using optimization method in MATLAB, and the activation energies (E_1 , E_2 and E_3) were determined by the Arrhenius equation. Furthermore, a kinetic model was developed.

Key words: Glycerol, Fuel additive, Esterification, Mixed oxide catalyst, Kinetics

1. Introduction

Rapid industrialization and economic development worldwide has created an overdependence on fossil fuels [1]. The unsustainable nature of the consumption of these fossil fuels has led to a shift in focus towards the development of greener fuels. This would help combat depleting energy reserves and environmental pollution globally [2]. Bio-diesel is a renewable fuel, having similar characteristics to petroleum [3]. This non-toxic, biodegradable, green alternative to diesel is synthesized by transesterification of vegetable oils (Soya bean oil, palm oil etc.) or animal fats with an alcohol [4-6]. Biodiesel fuel produced from biomass is clean as its combustion releases low amounts of carbon dioxide and no sulfurous or aromatic species. A global biodiesel market exists. Current production capacities have failed to satisfy demand, due to the formation of a considerable amount of byproduct, glycerol [7]. Glycerol can be converted into many value added products such as glycidol, oxygenated additives and syngas [8-10]. Among all the useful routes explored, esterification of glycerol with acetic acid is an effective way to utilize the glycerol. Mono-, di- and tri- esters called acetins are the products obtained. High-value oxygenated fuel additives are obtained from this reaction. Acetins are employed as food additives, solvents, safety plasticizers, softening agents, biodegradable polyesters and fuel additives [11-14].

Using a solid catalyst in place of a homogeneous catalyst results in

several shortcomings, namely, excessive catalyst usage, corrosion of equipment, lack of recyclability, difficulties in catalyst separation, reduced product purity and environmental hazards can now be overcome. Different metal oxides such as TiO_2 , Al_2O_3 , CeO_2 , SiO_2 , ZrO_2 , act as acid catalysts individually. Mixed oxides often show increased acidity and thermal stability than constituent single oxide. Some important properties of a mixed oxide that ensure it is an ideal catalyst include low cost, high stability towards water, activity over a wide range of temperatures, high selectivity and activity, increased surface area and the ease of regeneration [15-17]. Literature on the acetins synthesis shows that attempts were made with ion exchanges, zeolites, heteropoly acids and mixed oxides are synthesized by the co-precipitation method [18- 22]. From the literature it is evident that the synthesis of acetins by esterification of glycerol using combustion synthesized mixed oxides is not reported. The solution combustion method has various advantages, such as less time and energy usage and easy process. The mixed oxide ceria-alumina is taken in the present work because of high reactive sites. $\text{CeO}_2\text{-Al}_2\text{O}_3$ has certain advantages over single oxides, such as stronger metal-support interactions, higher acidity compared to single oxides, and better resistance to sintering. There are sporadic attempts in reporting the kinetics of the esterification of glycerol [23]. The main objective of this work was to synthesize $\text{CeO}_2\text{-Al}_2\text{O}_3$ by the combustion method and then sulfated to increase the acid site density on the surface of the catalyst. The sulfated cerium mixed oxide is used as a catalyst in the synthesis of acetins under varying temperatures, mole ratios and amounts of catalyst. The yield and selectivity of monoacetin, diacetin and triacetin are reported. Subsequently, based on the yield of products kinetic modeling was carried out for this reaction. The evaluated kinetic parameters (k_1 , k_2 and k_3) aid in the design and

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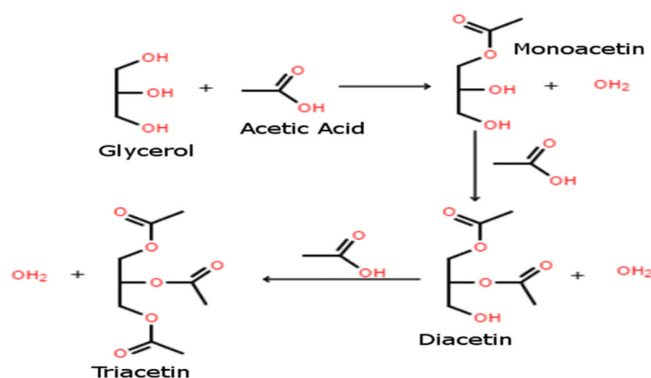
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scaling up of the reactors for the large-scale production of fuel additives.

1-1. Esterification of glycerol

The reaction of glycerol with acetic acid in the presence of an acid catalyst leads to the formation of acetins. The reaction follows a normal esterification mechanism and gives the series products monoacetin, diacetin and triacetin.



2. Materials and Methods

2-1. Chemicals

Cerium Nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), urea, sulfuric acid, glycerol and acetic acid were analytical grade and obtained from SD Fine Chemical Ltd.

2-2. Catalyst preparation

The desired mixed oxide catalyst ($\text{CeO}_2\text{-Al}_2\text{O}_3$) was synthesized by the combustion method. The requisite quantities of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and the stoichiometric quantity of solid urea ($\text{H}_2\text{N-CO-NH}_2$) as fuel were dissolved in distilled water and placed in a beaker. The mixture's composition was calculated on the basis of oxidizing valences of the oxidizer and the reducing valency of the fuel, i.e., metal nitrate to fuel valence ratio of 2.5. The aqueous solution containing redox mixture in a crucible was introduced into a muffle furnace which was preheated to 550 °C. The entire combustion process took about 20 minutes to produce the mixed oxide catalyst in open furnace. The synthesized catalyst was sulfated to introduce more active acid sites by adding 0.5 M sulfuric acid solution. The mixture of catalyst along with sulfuric acid was mechanically stirred for 1 hour at 300 rpm at room temperature. The sample was dried in a hot air oven at 120 °C for 3 hours and calcined at 300 °C for 2 hours.

2-3. Catalyst characterization

The XRD pattern of synthesized $\text{SO}_4^{2-}/\text{CeO}_2\text{-Al}_2\text{O}_3$ was recorded on a JDX-8030 XRD using copper $\text{K}\alpha$ (0.15418 nm) radiation source. The intensity data were collected over a 2θ range of 7-95° with a step size of 0.02°. The counting time was 1°/min. FTIR analysis involved using a Bruker Alpha FTIR spectrophotometer. A Smart Sob 92/93

BET surface area analyzer was used for analyzing the surface area. This is a single point surface area analyzer, and the analysis was carried out at a nitrogen partial pressure of 0.3. For SEM analysis, ESEM Quanta 200 instrument with tungsten based filament was used. Gold coating was carried out on the samples. The counts per second (CPS) were maintained above 600. The dead time was between 20-40 seconds.

2-4. Experimental Procedure for esterification of glycerol

The efficacy of the catalyst was studied for the esterification of glycerol with acetic acid using a three-necked flask containing a magnetic stirrer and a reflux condenser to prevent evaporation of reactants under atmospheric pressure. The reaction mixture was allowed to reach the desired reaction temperature, and then charged into the round bottom flask with the catalyst. Samples were withdrawn periodically and centrifuged for 5 min to separate the catalyst from liquid phase and cooled to below 5 °C to cease the reaction. The samples were further analyzed.

2-5. Analytical method

The obtained products were analyzed by gas chromatography (Agilent) with flame ionization detector (FID) equipped with capillary column (0.53 mm I.D and 30m length, Carbostable wax, Elite). The periodically collected samples were analyzed with a gas chromatograph. 0.5 ml of the sample was mixed with 50 ml of methanol. 0.5 μl of this solution was injected to the GC column that was maintained at a column temperature of 100 °C. The temperature was increased with a ramp input of 8 °C/min until it reached 220 °C. Nitrogen was used as the carrier gas.

$$\text{Yield (\%)} = \frac{\text{moles of product formed}}{\text{moles of glycerol feed}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{moles of desired product formed}}{\text{moles of total product formed}} \times 100$$

3. Results and Discussion

3-1. Catalyst characterization

XRD, FTIR, BET and SEM characterization was carried out for the catalyst and the results obtained are discussed below.

3-1-1. X-ray powder diffraction

Fig. 1 shows the XRD pattern with sharp peaks reflecting the crystalline form of $\text{CeO}_2\text{-Al}_2\text{O}_3$. The major diffraction peaks were observed at 2θ values of 29.3, 31, 48.6 and 58 for CeO_2 and Al_2O_3 . The peaks obtained were in accordance with the JCPDS-01-075-0390 for the cerium-aluminum mixed oxide, confirming the formation of the $\text{CeO}_2\text{-Al}_2\text{O}_3$ mixed oxide catalyst. The phase of the synthesized catalyst was identified to be of a fluorite structure using Profex software (Database of XRD patterns) as shown in Fig. 2. The peaks of synthesized catalyst coincide with green lines representing the fluo-

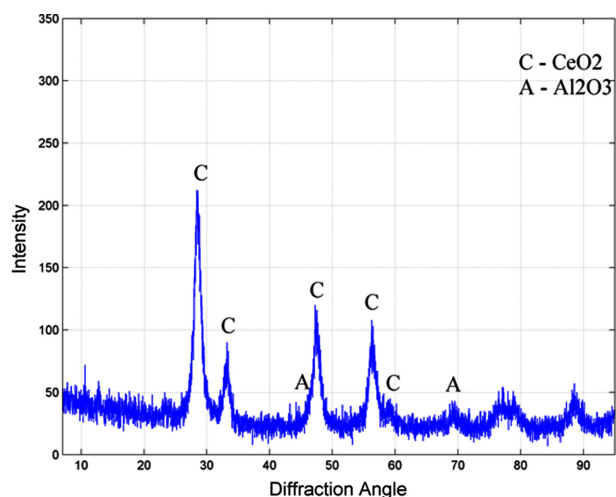


Fig. 1. X-ray diffraction pattern of $\text{CeO}_2\text{-Al}_2\text{O}_3$ representing CeO_2 and Al_2O_3 peaks.

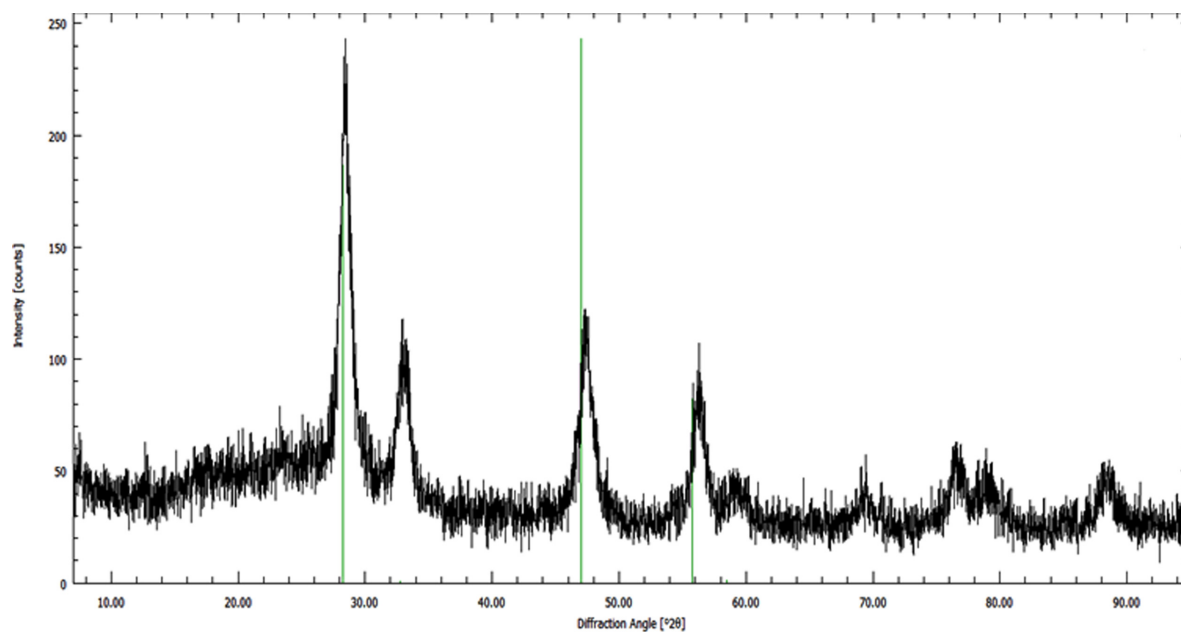


Fig. 2. X-ray diffraction pattern of $\text{CeO}_2\text{-Al}_2\text{O}_3$ coinciding with the fluorite structure lines.

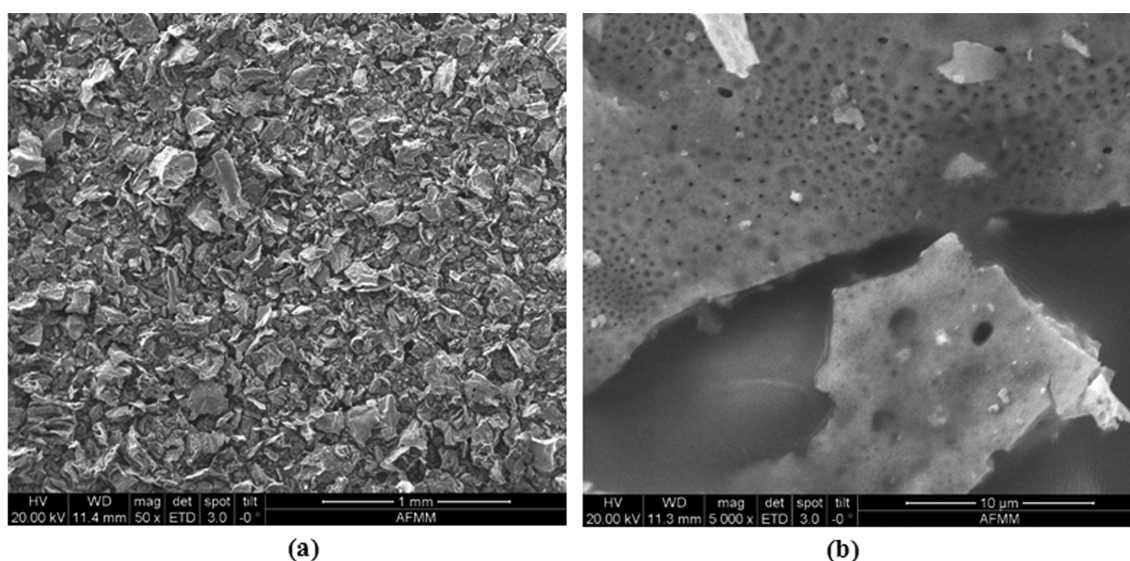


Fig. 3. SEM images of $\text{CeO}_2\text{-Al}_2\text{O}_3$.

rite lines confirming the fluorite phase of the catalyst.

3-1-2. BET surface area

The results of BET surface area of the samples showed that the specific surface area of $\text{CeO}_2\text{-Al}_2\text{O}_3$ was $9.5 \text{ m}^2/\text{g}$ and $\text{CeO}_2\text{-Al}_2\text{O}_3/\text{SO}_4^{2-}$ was $10.36 \text{ m}^2/\text{g}$. The increase in surface area upon impregnation with sulfate ions was due to the formation of pores between the sulfate ions and the base catalyst.

3-1-3. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) provided further insights into the morphology of the cerium oxide-aluminum oxide particles. Fig. 3a and 3b show the presence of particles of irregular morphology. Particles were of $10 \mu\text{m}$ size and some particles were of $0.2 \mu\text{m}$ size. The synthesized $\text{CeO}_2\text{-Al}_2\text{O}_3$ material has porous surface which

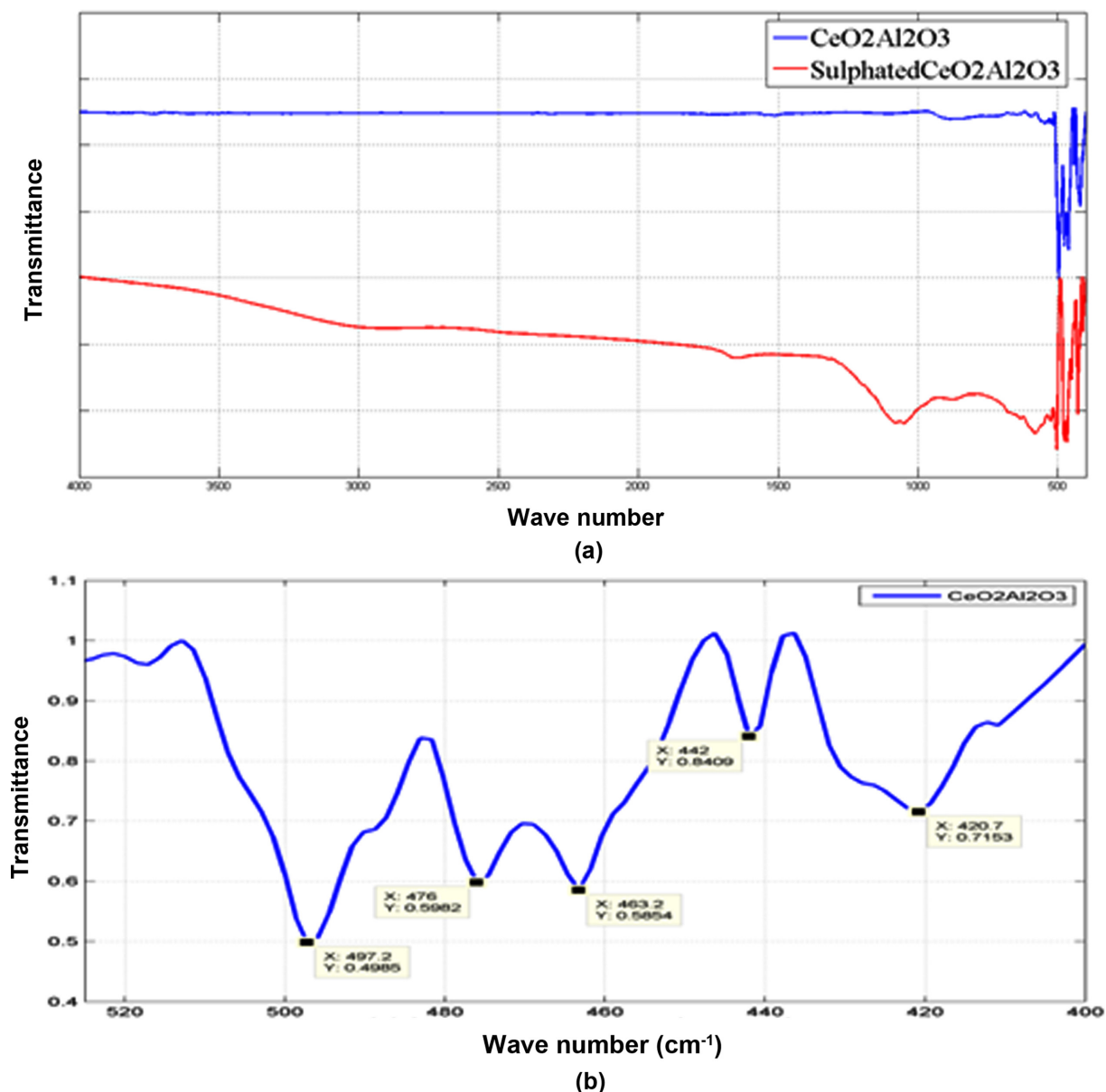


Fig. 4. FTIR Spectra of $\text{CeO}_2\text{-Al}_2\text{O}_3$ and $\text{CeO}_2\text{-Al}_2\text{O}_3/\text{SO}_4^{2-}$.

is caused by escaping gases during the synthesis of the catalyst.

3-1-4. Fourier-transform infrared spectroscopy

The FTIR spectra of $\text{CeO}_2\text{-Al}_2\text{O}_3$ and $\text{CeO}_2\text{-Al}_2\text{O}_3/\text{SO}_4^{2-}$ are shown in Fig. 4a and 4b. The presence of a peak at 497 cm^{-1} detects the presence of Ce-O, the peaks at 420 cm^{-1} and in between 500 and 450 cm^{-1} represent the presence of Al-O bond (Fig. 4b). The presence of a peak at 1111 cm^{-1} detects the presence of sulfate group (Fig. 4a).

3-2. Effect of process parameters

The synthesized sulfated $\text{CeO}_2\text{-Al}_2\text{O}_3$ was used as the catalyst for carrying out the esterification of glycerol. Acetic acid was always taken in excess over glycerol to shift the equilibrium towards the formation of acetins. The effects of temperature, concentration of reactants (mole ratio) and a catalyst amount were studied for the reaction.

3-3. Influence of reaction temperature on yield of products

The temperatures studied were $90\text{ }^\circ\text{C}$, $100\text{ }^\circ\text{C}$ and $110\text{ }^\circ\text{C}$ for the esterification of glycerol with acetic acid for a mole ratio (acetic acid to glycerol) of 6:1 and 5 wt% of catalyst for 3 hours. From Fig. 5a, 5b and 5c it can be observed that due to the increase in the rate of reaction, the conversion of glycerol increased with temperature. The maximum conversion of glycerol obtained was 87.5% at $110\text{ }^\circ\text{C}$ and 25% yield of triacetin was obtained. From Fig. 6, the selectivity towards diacetin and triacetin is higher at $110\text{ }^\circ\text{C}$, whereas the selectivity of monoacetin has decreased.

3-4. Influence of mole ratio (acetic acid: glycerol) on yield of products

The mole ratio (acetic acid: glycerol) was varied from (3:1 to 9:1) for esterification of glycerol with acetic acid at reaction temperature

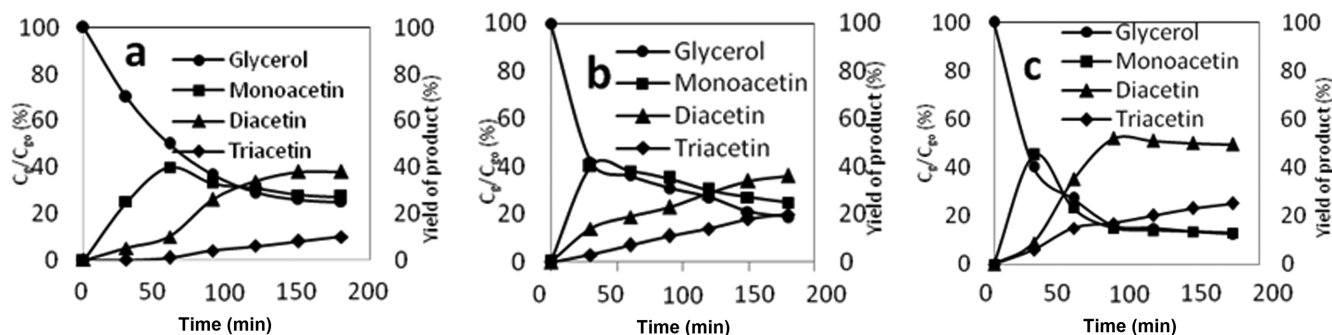


Fig. 5. Effect of different temperature: (a) 90 °C, (b) 100 °C, (c) 110 °C on the product distribution of glycerol esterification (catalyst loading= 5 wt% and Acetic acid: glycerol 6:1).

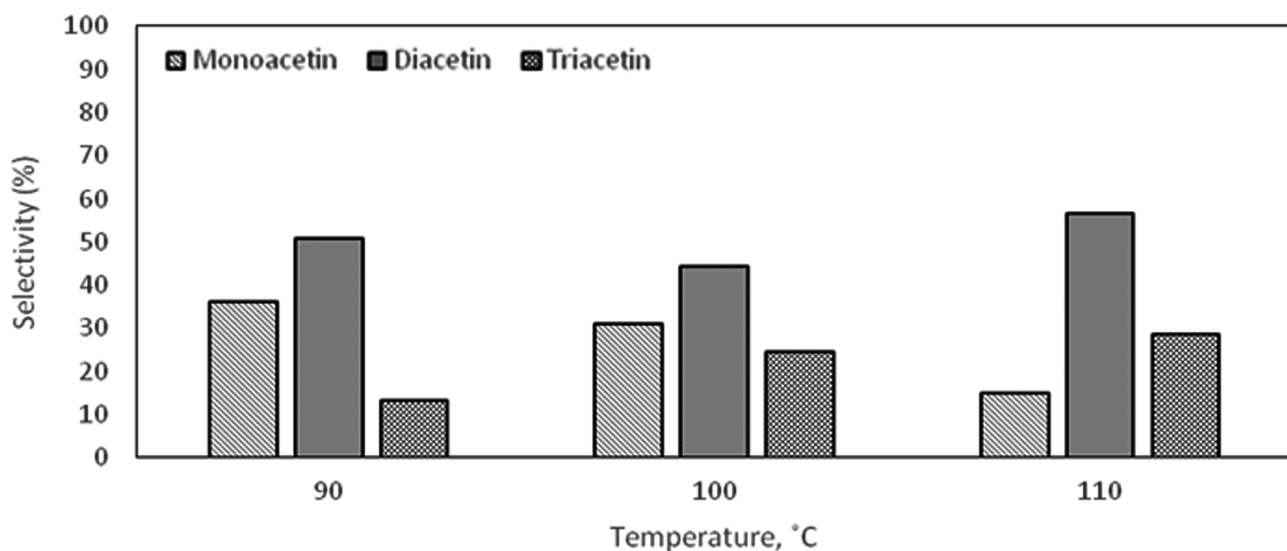


Fig. 6. Percentage selectivity of products for various reaction temperatures (catalyst loading= 5 wt% and Acetic acid: glycerol 6:1).

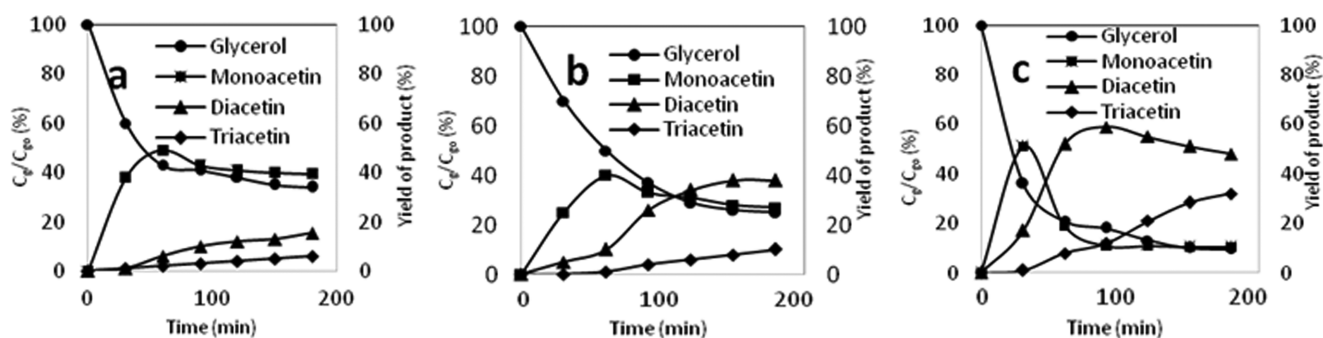


Fig. 7. Effect of different mole ratio of acetic acid: glycerol: (a) 3:1, (b) 6:1, (c) 9:1 on the product distribution of glycerol esterification (catalyst loading= 5 wt% and reaction temperature 110 °C).

of 110 °C and 5wt% of catalyst for 3 hours. Since esterification is a reversible reaction, the use of excess acetic acid shifts the equilibrium towards the products. From Fig. 7a, 7b and 7c it can be observed that with an increase in the mole ratio of acetic acid from 3:1 to 9:1 the conversion of glycerol also increased due to excess concentration of acetic acid. Along with the increase in conversion of glycerol, the yield of acetins also increased. The maximum conversion of 90.5% for glycerol and maximum yield of 32% for triacetin was

obtained at 110 °C for 3 hours for 9:1 acetic acid: glycerol. Fig. 8 shows that the selectivity towards diacetin and triacetin is higher for 9:1 of acetic acid: glycerol. The selectivity towards monoacetin is high at 3:1.

3-5. Influence of catalyst loading on yield of products

The catalyst weight percentage studied was 1 wt%, 3 wt% and 5 wt% on esterification of glycerol with acetic acid for mole ratio of

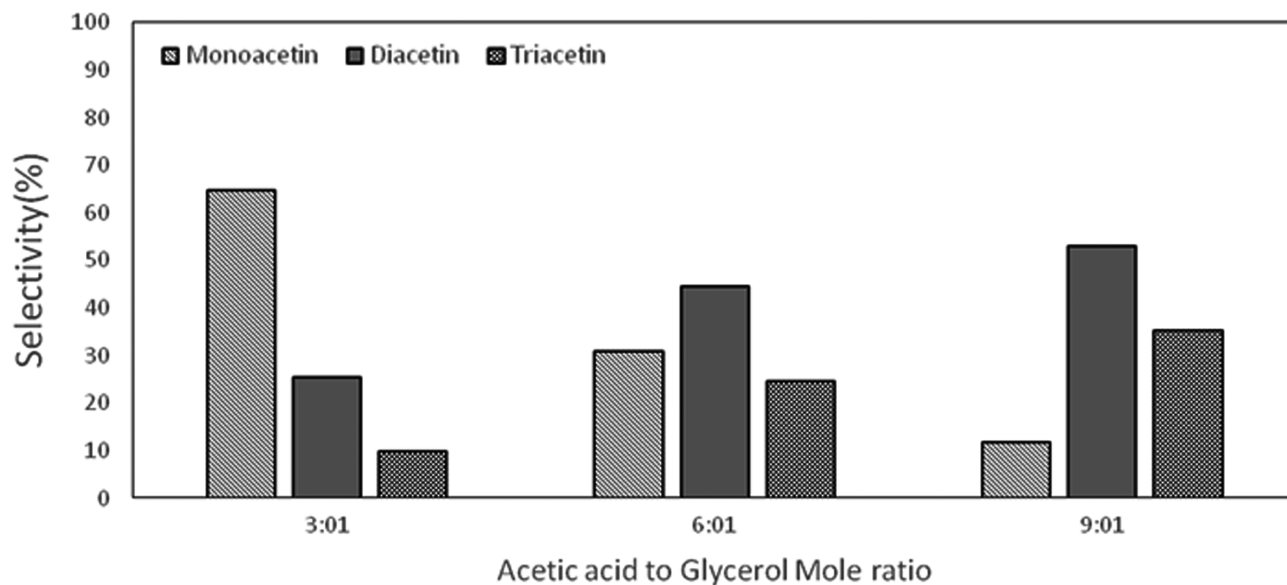


Fig. 8. Percentage selectivity of products for different mole ratio after 3 hours (catalyst loading= 5 wt% and reaction temperature 110 °C).

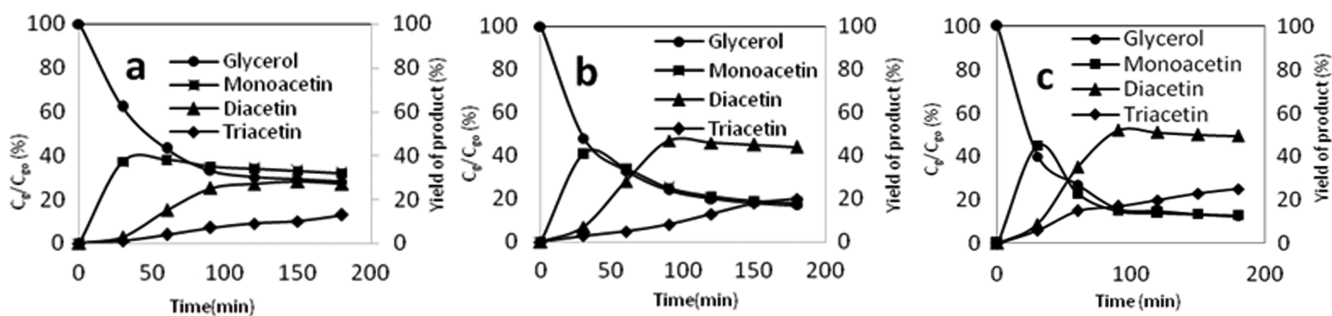


Fig. 9. Effect of different catalyst loading: (a) 1 wt%, (b) 3 wt%, (c) 5 wt% on the product distribution of glycerol esterification (molar ratio acetic acid: glycerol 6:1 and reaction temperature 110 °C).

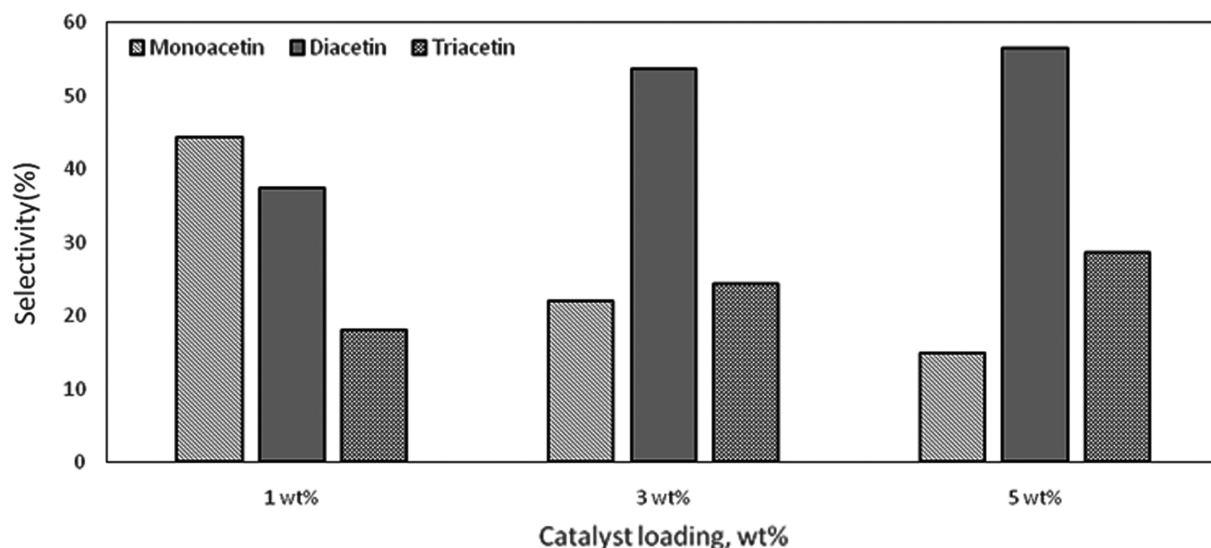


Fig. 10. Percentage selectivity of products for various catalyst loading (reaction temperature 110 °C and Acetic acid: glycerol 6:1).

reactants (acetic acid : glycerol) 6:1 at reaction temperature of 110 °C for 3 hours. Fig. 9a, 9b and 9c reflect the influence of catalyst loading on the products yield and glycerol conversion, and clearly indi-

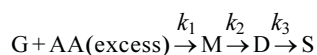
cate that this is due to relative increase in the number of active sites. The maximum conversion of 87.5% for glycerol and maximum yield of 25% for triacetin was obtained for 5wt% catalyst loading at

110 °C after 3 hours. Fig. 10 shows that the selectivity towards diacetin and triacetin is higher for 5 wt%. The selectivity towards monoacetin is high at 1 wt%.

3-6. Reaction Kinetics

The Langmuir-Hinshelwood kinetics model was used to express the rate law for glycerol esterification with acetic acid. The model assumes that there is a weak adsorption of both reactants and products on the surface of catalyst with surface reaction being the rate determining step. It can be further justified that the resistance term of the LHHW model could be ignored [23].

Due to excess supply of acetic acid over glycerol, the glycerol esterification reaction drives in forward direction for products before equilibrium, and the backward reaction in each step can be neglected for developing the kinetics. Hence, the glycerol esterification can be represented as homogeneous irreversible first-order reactions in series.



where G = glycerol, AA= acetic acid, M = monoacetin, D = diacetin and S = triacetin.

For a batch reactor under isothermal conditions, the above mechanism gives the following unsteady - state material. The reaction rate expression of different species can be written as:

$$-r_G = \frac{-dC_G}{dt} = k_1 C_G$$

Let $Y = C_i/C_{G0}$ $i = G, M, D, S$

Slope of the curve, $-dY_G/dt$ at each Y_G , is calculated. The value of k_1 is determined using interpolation method.

$$-r_E = \frac{dC_M}{dt} = k_1 C_G - k_2 C_M$$

Slope of the curve, $-dY_M/dt$ at each Y_G , is calculated. The value of k_1 which is determined above is used and k_2 is determined using interpolation method.

$$-r_D = \frac{-dC_D}{dt} = k_2 C_M - k_3 C_D$$

Slope of the curve $-dY_D/dt$ at each Y_D , is calculated. The value of k_2 which is determined above is used and k_3 is determined using interpolation method.

The r_G , r_M and r_D are the reaction rates (mol/min·L) of species G, M and D; C_G , C_M and C_D are the concentration (mol/L) of species G, M and D and t at any time in the reactor, respectively.

The rate constants were evaluated using an optimization method (MATLAB) at different temperatures. The temperature dependency of the rate constants can be expressed using the Arrhenius equation. Considering the overall apparent rate constants (k_1 , k_2 and k_3),

$$k_i = k_{i0} e^{(-\Delta E/RT)}$$

or

$$\ln(k_i) = \ln(k_{i0}) - \frac{\Delta E}{RT}$$

where $i = 1, 2, 3$ and k_{i0} is the frequency factor.

Plots of $\ln(k_i)$ versus $1/T$ are shown in Fig. 11a, 11b and 11c, and the activation energies were determined from the slope of the graph.

The apparent rate constants (k_1 , k_2 and k_3) and activation energies (E_1 , E_2 and E_3) for acetic acid to glycerol mole ratio 6:1 and at 5 wt% catalyst are represented as:

$$k_1 = \exp(7.6639 - \frac{4393.9}{T}); E_1 = 36.52 \text{ kJ/mol}; R^2 = 0.9888$$

$$k_2 = \exp(6.4327 - \frac{4035}{T}); E_2 = 33.55 \text{ kJ/mol}; R^2 = 0.9741$$

$$k_3 = \exp(3.4284 - \frac{3410.4}{T}); E_3 = 28.35 \text{ kJ/mol}; R^2 = 0.9891$$

3-7. Comparison of $SO_4^{2-}/CeO_2-Al_2O_3$ with reported catalyst for esterification of glycerol

The present catalyst $SO_4^{2-}/CeO_2-Al_2O_3$ was compared to that of the catalyst reported in literature. Among the reported catalyst Amberlyst -35 showed a higher glycerol conversion of 99% and triacetin selectivity of 25%, HZSM-5 achieved 30% glycerol conversion, K-10 attained 95% glycerol conversion with 5% triacetin selectivity at different reaction conditions. The $SO_4^{2-}/CeO_2-Al_2O_3$ attained 90.5% for glycerol conversion, and selectivity of 32% for triacetin was obtained at 110 °C for 3 hours for 9:1 acetic acid: glycerol.

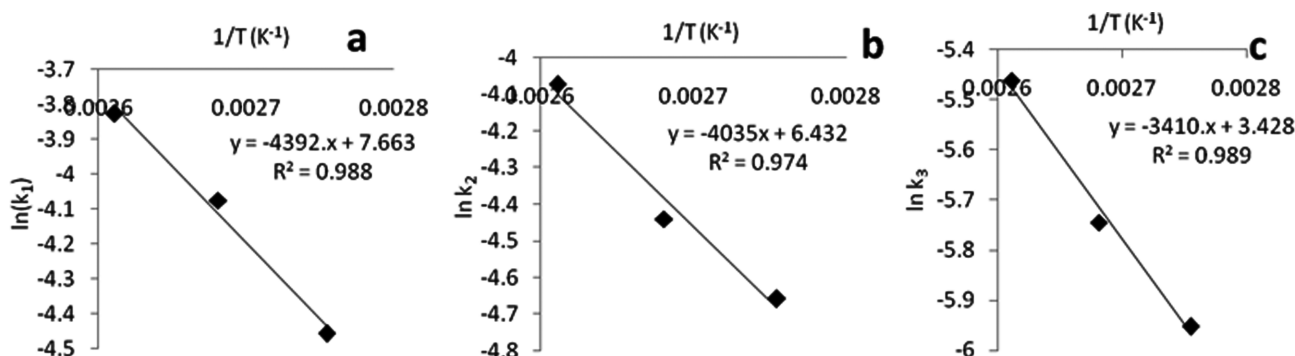


Fig. 11. Plot of (a) $\ln k_1$ vs $1/T$, (b) $\ln k_2$ vs $1/T$, (c) $\ln k_3$ vs $1/T$.

4. Conclusion

An ecofriendly catalytic process was developed for the synthesis of acetins from esterification of glycerol using $\text{CeO}_2\text{-Al}_2\text{O}_3/\text{SO}_4^{2-}$. The catalyst was characterized to understand its activity. The effect of yield and selectivity of products was checked under varied molar ratios of acetic acid to glycerol, temperature and amount of catalyst. The reaction followed homogeneous pseudo first-order series reaction. The rate constants (k_1 , k_2 and k_3) as well as conforming activation energy (E_1 , E_2 and E_3) were found.

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