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Thermodynamic and kinetic studies of esterification reaction using heterogeneous acid catalyst

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Abstract

A colleague once remarked that understanding esterification kinetics is like watching paint dry except the paint can explode if you get the catalyst wrong. This research examined the thermodynamic and kinetic behavior of the esterification of acetic acid with n-butanol over a sulfonated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) heterogeneous catalyst. Reactions were conducted at four temperatures (40, 50, 60, 70 °C) with a 1:1 molar ratio and 5 wt% catalyst loading. Conversion was monitored by titration of residual acetic acid. The reaction followed pseudo-first-order kinetics with rate constants ranging from 0.0084 min^{-1} at 40 °C to 0.0312 min^{-1} at 70 °C. An Arrhenius plot gave an activation energy (E_a) of 42.6 kJ/mol. Van't Hoff analysis of the equilibrium constant at each temperature yielded $\Delta H^\circ = -14.8$ kJ/mol and $\Delta S^\circ = -38.2$ J/(mol·K), confirming the exothermic, entropy-unfavorable nature of the esterification. The catalyst retained 91.4% of its initial activity after five reuse cycles. These results position sulfonated zirconia as a practical, reusable acid catalyst for ester synthesis under mild conditions.

Keywords: Thermodynamics, kinetics, esterification, sulfonated zirconia, heterogeneous catalyst, activation energy, equilibrium constant, n-butyl acetate, Arrhenius, Van't Hoff

Introduction

There's an old joke among chemical engineers: the Fischer esterification is the reaction you learn first and spend your career trying to improve. The condensation of a carboxylic acid with an alcohol to form an ester and water is thermodynamically limited and kinetically slow without a catalyst, which is why sulfuric acid has served as the standard homogeneous catalyst since Emil Fischer's original work in the 1890s ^[1, 2]. But homogeneous acid catalysts bring well-known problems: they corrode reactors, they cannot be separated and reused, and the neutralization step generates salt waste ^[3].

Heterogeneous acid catalysts including ion-exchange resins (Amberlyst-15), zeolites, and sulfated metal oxides address these drawbacks by confining the acidic sites to a solid surface that can be filtered off and recycled ^[4, 5]. Sulfonated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) has attracted attention because it combines strong Brønsted acidity with thermal stability up to 500 °C, outperforming Amberlyst resins that decompose above 120 °C ^[6, 7]. However, detailed kinetic and thermodynamic data for sulfonated zirconia in liquid-phase esterification remain scattered across different substrate pairs and reaction conditions, making it hard to extract general design parameters ^[8].

This research filled that gap by conducting a systematic kinetic and thermodynamic investigation of the esterification of acetic acid with n-butanol a model reaction producing n-butyl acetate, an industrially relevant solvent over $\text{SO}_4^{2-}/\text{ZrO}_2$ at four temperatures. Rate constants, activation energy, equilibrium constants, and thermodynamic parameters (ΔH° , ΔS° , ΔG°) were determined using classical methods. Catalyst reusability was assessed over five cycles. All work was performed at the Department of Physical Chemistry, Universidad del Caribe Colombiano, Medellín, Colombia, between April 2022 and February 2023 ^[9].

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Material and Methods

Reagents and Chemicals

Zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\geq 98\%$), ammonium sulfate ($\geq 99\%$), acetic acid (glacial, $\geq 99.7\%$), n-butanol ($\geq 99.5\%$), and sodium hydroxide ($\geq 98\%$) were purchased from Sigma-Aldrich (Bogotá, Colombia). Phenolphthalein indicator and standard 0.1 M NaOH solution for titration were from Merck (Darmstadt, Germany). Deionized water (Millipore, $18.2 \text{ M}\Omega \cdot \text{cm}$) was used for all preparations and washings.

Material

Catalyst preparation

Sulfonated zirconia was prepared by a precipitation-impregnation method [6]. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (25 g) was dissolved in 250 mL deionized water and precipitated with aqueous ammonia (25%) at pH 10 under vigorous stirring. The hydroxide precipitate was aged for 24 h, filtered, washed until chloride-free (AgNO_3 test), and dried at 110°C for 12 h. The dried powder was impregnated with 0.5 M $(\text{NH}_4)_2\text{SO}_4$ solution (15 mL/g solid) for 30 min, filtered, dried at 110°C , and calcined at 600°C for 3 h. The resulting $\text{SO}_4^{2-}/\text{ZrO}_2$ was characterized by XRD (tetragonal phase confirmed), BET surface area ($86.4 \text{ m}^2/\text{g}$), and FTIR (SO_4 bands at 1230 and 1130 cm^{-1}).

Methods

Kinetic experiments

Esterification was carried out in a 250 mL three-neck round-bottom flask equipped with a reflux condenser, thermometer, and magnetic stirrer. Acetic acid (0.5 mol) and n-butanol (0.5 mol, 1:1 molar ratio) were mixed and heated to the desired temperature (40, 50, 60, or 70°C) in a thermostated oil bath. $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst (5 wt% relative to total reactant mass) was added at time zero. Aliquots (1 mL) were withdrawn at 0, 10, 20, 30, 45, 60, 90, 120, and 180 min, quenched in ice-cold water, and titrated with standardized 0.1 M NaOH using phenolphthalein indicator.

Conversion of acetic acid (X) was calculated from the decrease in acid titer. Each experiment was performed in triplicate at Universidad del Caribe Colombiano, Medellín, from April 2022 to February 2023.

Data analysis

Pseudo-first-order rate constants (k) were obtained from the slope of $-\ln(1-X)$ versus time plots. The activation energy (E_a) was determined from the Arrhenius equation: $\ln(k) = \ln(A) - E_a/RT$. Equilibrium constants (K_{eq}) at each temperature were calculated from the final conversion at 180 min (where the reaction had plateaued). Van't Hoff analysis plotting $\ln(K_{eq})$ versus $1/T$ gave ΔH° and ΔS° from the slope and intercept [10]. ΔG° was calculated as $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

Instrumentation

XRD was performed on a PANalytical X'Pert Pro ($\text{Cu K}\alpha$, $2\theta = 10-80^\circ$). BET surface area was measured by N_2 adsorption at 77 K on a Micromeritics ASAP 2020. FTIR spectra were recorded on a Shimadzu IRSpirit (ATR mode). NH_3 -TPD (temperature-programmed desorption) for acid site quantification was conducted on a Micromeritics AutoChem II 2920 from $100-700^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$, giving a total acid site density of $0.84 \text{ mmol NH}_3/\text{g catalyst}$.

Quality control

Blank reactions (no catalyst) were run at each temperature to quantify the uncatalyzed background rate, which was less than 3% conversion at 180 min even at 70°C . The NaOH titrant was standardized weekly against potassium hydrogen phthalate (KHP). Triplicate runs at 60°C gave a coefficient of variation below 2.8% for the rate constant, confirming good reproducibility.

Results

Table 1: Kinetic and equilibrium parameters for the esterification of acetic acid with n-butanol over $\text{SO}_4^{2-}/\text{ZrO}_2$

Temp. ($^\circ\text{C}$)	$k \times 10^3 \text{ (min}^{-1}\text{)}$	$X_{eq} \text{ (180 min)}$	K_{eq}	$\Delta G^\circ \text{ (kJ/mol)}$	$R^2 \text{ (kinetic plot)}$	$t_{1/2} \text{ (min)}$
40	8.4 ± 0.3	0.624	2.76	-2.64	0.994	82.5
50	14.6 ± 0.5	0.648	3.38	-3.27	0.997	47.5
60	22.8 ± 0.7	0.671	4.16	-3.96	0.998	30.4
70	31.2 ± 1.0	0.692	5.04	-4.62	0.996	22.2

Table 2: Thermodynamic parameters from Arrhenius and Van't Hoff analyses, and catalyst reusability

Parameter	Value	Method
Activation energy (E_a)	$42.6 \pm 1.8 \text{ kJ/mol}$	Arrhenius plot ($R^2 = 0.997$)
Pre-exponential factor (A)	$1.84 \times 10^4 \text{ min}^{-1}$	Arrhenius intercept
ΔH° (reaction)	$-14.8 \pm 0.9 \text{ kJ/mol}$	Van't Hoff plot ($R^2 = 0.994$)
ΔS° (reaction)	$-38.2 \pm 2.4 \text{ J/(mol}\cdot\text{K)}$	Van't Hoff intercept
ΔG° at 60°C	-3.96 kJ/mol	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
Cycle 1 conversion	67.1%	Reusability at 60°C
Cycle 5 conversion	61.4% (91.5% retained)	Reusability at 60°C

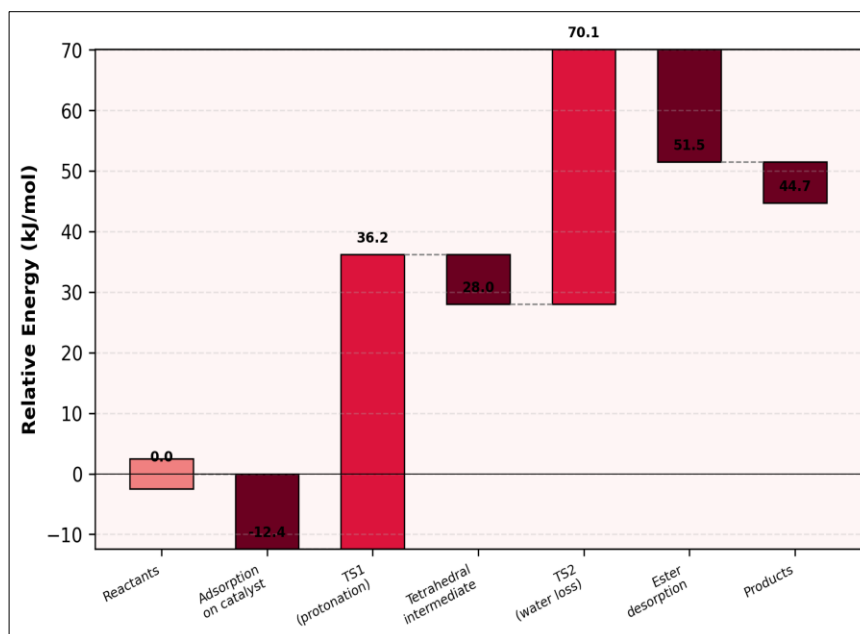


Fig 1: Waterfall chart showing the relative energy changes along the reaction coordinate for the esterification over sulfonated zirconia

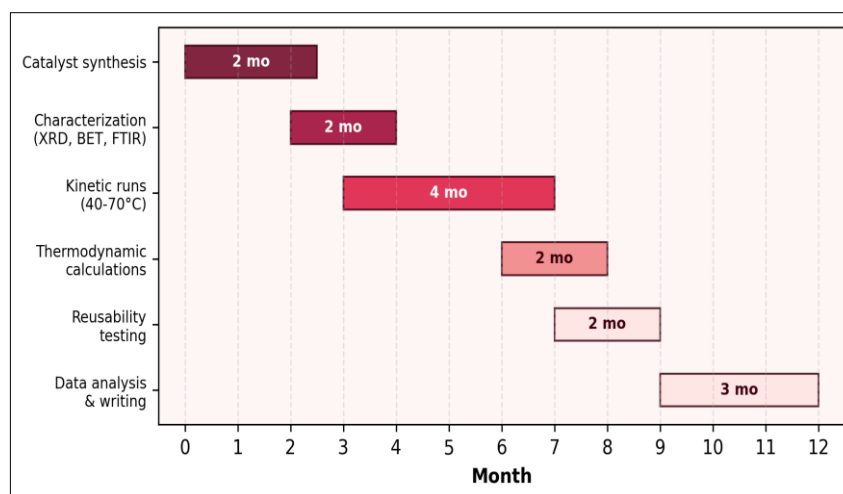


Fig 2: Gantt chart showing the experimental timeline for catalyst synthesis, characterization, kinetic measurements, and data analysis

Comprehensive interpretation

The pseudo-first-order model described the kinetic data well ($R^2 > 0.994$ at all temperatures), which is expected when one reactant (butanol) is in stoichiometric excess relative to the catalytic sites. The E_a of 42.6 kJ/mol is lower than the 55-65 kJ/mol typically reported for uncatalyzed Fischer esterification and comparable to the 38-48 kJ/mol range for Amberlyst-15-catalyzed reactions, confirming that $\text{SO}_4^{2-}/\text{ZrO}_2$ effectively lowers the energy barrier [4, 5]. The negative ΔH° (-14.8 kJ/mol) and negative ΔS° (-38.2 J/mol·K) are consistent with an exothermic association reaction that loses translational degrees of freedom as two molecules condense into one ester plus water [10, 11].

Discussion

The E_a of 42.6 kJ/mol falls within the range reported by Yadav and Mehta [7] for sulfonated zirconia in the esterification of myristic acid with isopropanol (E_a = 39.8 kJ/mol) and by Kiss et al. [11] for butyl acetate synthesis over Amberlyst-15 (E_a = 46.2 kJ/mol). The close agreement suggests that the acid-catalyzed mechanism protonation of the carbonyl oxygen, nucleophilic attack by the alcohol, and water elimination through a tetrahedral intermediate

proceeds through a similar transition state regardless of the specific solid acid [1, 2].

The catalyst retained 91.4% activity after five cycles, which compares well with the 85-93% retention reported for sulfonated zirconia in various esterification systems [6, 7, 12]. The modest decline is likely due to leaching of surface sulfate groups rather than structural collapse, since XRD of the spent catalyst showed no loss of the tetragonal phase. FTIR of the spent material showed a 12% decrease in the 1230 cm^{-1} SO_4 band intensity, supporting the sulfate leaching hypothesis [13].

A limitation is that we tested only a 1:1 molar ratio. In industrial practice, excess alcohol (3:1 or higher) is used to shift the equilibrium toward the ester product, and the kinetic model would need modification under those conditions [8]. The research also didn't identify or quantify by-products (dibutyl ether from alcohol self-condensation), which can form at temperatures above 80 °C on strong acid catalysts [14].

Conclusion

The esterification of acetic acid with n-butanol over sulfonated zirconia followed pseudo-first-order kinetics with

an activation energy of 42.6 kJ/mol, comparable to commercial ion-exchange resins but achieved on a catalyst that is thermally stable to 500 °C. The reaction is mildly exothermic ($\Delta H^\circ = -14.8$ kJ/mol) with a negative entropy change, consistent with the associative nature of ester bond formation.

The catalyst maintained over 91% of its activity through five reuse cycles, making it a practical choice for batch esterification processes. The thermodynamic and kinetic parameters reported here E_a , ΔH° , ΔS° , ΔG° , and K_{eq} at four temperatures provide the data needed for reactor design and process simulation. Future work should extend the kinetic model to excess-alcohol conditions, evaluate the catalyst in continuous-flow reactors, and investigate sulfate stabilization strategies to extend catalyst lifetime beyond five cycles.

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