Original Article

Kinetics and mechanism of Pechmann condensation reaction over sulphated zirconia-supported zinc oxide

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ABSTRACT

An investigation of the kinetics of the Pechmann condensation reaction over ZnO supported on sulphated zirconia (ZnO/SZ) catalyst has been performed. The ZnO/SZ catalyst contains both Lewis (L) and Brønsted (B) acid sites. The maximum B/L ratio was obtained with a ZnO content of 6%. The reaction is first-order half in both acetoacetate and resorcinol, which supports the proposed reaction mechanism. The reaction temperature was found to have a great effect on the kinetics of coumarin synthesis, and the activation energy was determined to be 42.29 kJ mol⁻¹. The experimental activation parameters for the reaction were calculated to be ΔH* = 39.20 kJ mol⁻¹, ΔS* = −152.62 J mol⁻¹ K⁻¹ and ΔG* = 99.18 kJ mol⁻¹ at 393 K. The negative value of the activation entropy (ΔS*) indicates that the entropy decreases upon forming the transition state, which proves that the transition state is more highly ordered than the reactants.

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1. Introduction

Solid-acid catalysts, especially metal oxide catalysts, are of great significance in a wide variety of catalytic processes important in the chemical industry [1]. Their favourable activities and selectivities have been attributed mostly to the presence of suitable amounts of Lewis and Brønsted acid sites. Sulphated metal oxides (SMO₃), including ZrO₂, SnO₂, TiO₂ and Fe₂O₃, possess both Brønsted acid sites (BASs) derived from the sulphates present on the surface of the catalyst and Lewis acid sites (LASs) derived from the metal oxides.

SMO₃ have been widely used as solid-acid catalysts in various organic transformations because of their high efficiency, non-toxicity, non-corrosiveness, low cost, high stability at elevated temperatures, and resistance to deactivation [2–5]. They can also be easily separated from reaction mixtures by simple filtration and reused after activation [6–8]. In the case of modified sulphated zirconia catalysts, doping with active metal species can also enhance their activity by improving crystallinity, acidity and particle size. Modified sulphated zirconia has been used to effectively catalyse condensation reactions for organic materials such as coumarins [9].

Coumarin, a benzoic acid derivative, is a natural compound commonly found in natural species, especially in green plants and some fungi [10,11]. Coumarin and its derivatives have been extensively used as laser dyes [12,13], fluores-
cent indicators [14,15] and photosensitizers [16,17]. Recently, coumarins have attracted great interest in synthetic organic chemistry due to their noticeable biological activities such as antibacterial [18,19], anticancer [20–22], antitumour [23], anti-Alzheimer [24], anti-HIV [25], antimicrobial [26,27], anti-inflammatory [28,29], and antioxidant activities [30–32]. The Perkin reaction, developed in 1863, was the first method for synthesizing coumarin derivatives [33]. In the 1990s, the Knoevenagel reaction provided a remarkable synthetic method for preparing coumarin derivatives with a carbonylic acid substituent at the 3-position [34,35]. Among all the procedures for coumarin synthesis, the Pechmann condensation is thought to be the most widely utilized technique as it proceeds with very simple starting reactants and produces several coumarin derivatives in good yields [36–38]. The Pechmann condensation to form 7-hydroxy-4-methyl coumarin from resorcinol and ethyl acetoacetate (EAA) was suggested to follow a three-step mechanism: transesterification, intramolecular hydroxyl alkylation, and dehydration, as shown in Scheme 1 [39]. The mechanism depends on proton transfer to the keto group of EAA from the acid sites of the catalyst by the interaction between EAA and the catalyst, and then an intermediate and ethanol are produced due to nucleophilic attack by a hydroxyl group of resorcinol. The intermediate rapidly cyclizes through an intramolecular condensation to yield 7-hydroxy-4-methyl coumarin [40]. The reaction mechanism has been studied via several theoretical methodologies. Among those, density functional theory (DFT) with a hybrid functional has been found to be effective in addition to offering sufficient precision at a suitable cost. The B3LYP functional was utilized to investigate the vibrational and chemical shifts of different coumarin derivatives [41–43]. The M05-2X functional was used to study the Pechmann reaction between esters and phenol [44]. PCM-TDDFT was used to examine the acid dissociation constants (pKa) of excited coumarin [45]. Recently, the M06-2X functional was efficiently used to determine the optical spectra of coumarins [46].

In this study, the catalytic performance of ZnO/SZ for the Pechmann condensation reaction was examined. The crystallinity and acid properties of the ZnO/SZ catalyst were investigated utilizing X-ray powder diffractometry (XRD), energy dispersive X-ray (EDX) and pyridine-FTIR techniques. The rates of the reaction at different reaction temperatures ranging from 353 K to 393 K were experimentally calculated and then fitted into the Arrhenius equation to measure the apparent activation energy. Additionally, different thermodynamic parameters were also determined through transition state theory.

2. Experimental

2.1. Materials

Zirconium nitrate (Zr(NO3)4), zinc nitrate (Zn(NO3)2·6H2O, 98%), distilled water, sulphuric acid [AnalR], resorcinol (C10H8O2, 99%), and ethyl acetoacetate (C4H6O3, 99%) were purchased from Sigma-Aldrich. Chemicals were used without further purification.

2.2. Preparation of sulphated zirconia (SZ)

Sulphated zirconia, the SZ catalyst, was prepared as follows: 17.5 g of zirconium nitrate was dissolved in 400 mL of distilled water with stirring. Sulphuric acid (2 N) was added dropwise to the zirconium solution with vigorous and continuous stirring at room temperature until a white gel had formed. The obtained white gel was dried on a rotary evaporator at 90 °C. Finally, the dried powder was calcined at different calcination temperatures (400, 500, 600, and 800 °C) for 3 h with a heating rate of 20 °C min⁻¹ [47].

2.3. Preparation of zinc oxide-doped sulphated zirconia (ZnO/SZ)

Zinc-doped sulphated zirconia, denoted ZnO/SZ, was synthesized by a simple impregnation method [47]. SZ was impregnated in a zinc nitrate solution. The amounts of zinc nitrate were calculated to give 4, 6, 8, 10, and 20 wt% ZnO. The appropriate amounts of zinc nitrate were dissolved in 50 mL of distilled water and then added dropwise to the above white gel under continuous stirring. The mixture was stirred magnetically for 2 h and then dried on a rotary evaporator at 90 °C. The synthesized samples were calcined at 400, 500, 600 and 800 °C for 3 h at a heating rate of 20 °C min⁻¹.

2.4. Characterization

2.4.1. XRD analysis

The powder X-ray diffraction (PXRD) patterns were recorded on an X-ray powder diffractometer (XRD) PW 150 (Philips) using Ni-filtered Cu Kα radiation (λ = 1.540 Å) at 40 kV and 30 mA over a scanning range 2θ of 18°–80°. The tetragonal phase of SZ was evaluated by the following equation [48].

\[
\text{Tetragonal} = \frac{\text{It}(2\theta = 30.15)}{\text{It}(2\theta = 30.15) + \left( \frac{\text{Im}(\theta - 28.16 \cdot \text{Im}(\theta - 31.44))}{2} \right)}
\]

The crystallite size (nm) was determined by the reflection of the SZ tetragonal phase at 2 h of 30.15 by the Scherrer equation [49,50]

\[ D = \frac{k\lambda}{\beta\cos\theta} \]

Where k is the crystallite shape constant (=1), λ is the radiation wavelength (Å), β is the line breadth (radians) and θ is the Bragg angle.

2.4.2. EDX analysis

Energy dispersive X-ray (EDX) spectroscopy was applied to determine the chemical composition of the catalysts. EDX analyses were conducted using an energy dispersive X-ray spectrometer connected to a scanning electron microscope [47].

2.4.3. FT-IR spectrometry with adsorbed pyridine

The Lewis and Brønsted acid sites on the catalyst surface were measured at room temperature by FT-IR analysis with adsorbed pyridine [51]. Before pyridine adsorption, each catalyst was activated at 120 °C for approximately 1 h. Dry pyridine was then flashed inside the vacuum system, and the cata-
lysts were maintained under these conditions for a sufficient amount of time. Then, the excess pyridine was removed by evaporation. The FT-IR spectra of the samples were recorded using a Mattson 5000 FT-IR spectrophotometer at room temperature by combining 0.05 g of the catalyst with 0.1 g of KBr to afford a self-supporting disc 30 mm in diameter [52].

2.4.4. Kinetics investigation of the Pechmann condensation reaction

The investigated reaction was carried out under reflux conditions. A mixture of resorcinol (which is considered a highly activated phenol and allows the reaction to be performed under much milder conditions) and ethyl acetoacetate was refluxed in the presence of freshly calcined catalyst; the reflux time and the amount of catalyst were varied to optimize the yield of coumarin [53,54]. Freshly calcined ZnO/SZ catalyst (0.1 g) was added, the mixture was refluxed for 2 h, and then the contents of the flask was poured onto crushed ice and scratched until the solid product was obtained [52,55].

The solid product was separated by filtration, dried and then extracted with hot ethanol. 7-Hydroxy-4-methyl coumarin was recovered from the alcoholic solution by evaporating the solvent in a hot water bath. The yield was determined by FT-IR (KBr, ν cm⁻¹): 3504 (O→H), 3110 (s=C–H), 1672 (C=O), 1600–1400 (C=C), 1392 (–CH₃) and 840–790 (tri-substituted alkene), which are characteristic of 7-hydroxy-4-methyl coumarin.

The order of the reaction was investigated by varying the reactant concentration in a systematic way. The activation energy can be experimentally calculated from the relation between the rate constant and different temperatures (353–393 K), which can be explained by the Arrhenius equation as given in Eq. (1):

\[ K = A e^{-Ea/RT} \] 

where \( k \) is the rate constant, \( A \) is the Arrhenius constant, \( E_a \) is the activation energy, \( R \) is the gas constant, and \( T \) is the temperature.

Activation enthalpy, entropy and free energy can be determined from the Eyring-Polanyi equation, which depends on transition state theory, as shown in Eq. (2):

\[ K = \frac{k_B T}{h} e^{-ΔS^*/R} e^{-ΔH^*/RT} \] 

where \( k \) is the rate constant, \( ΔH^* \) is activation enthalpy (kJ mol⁻¹), \( ΔS^* \) is activation entropy (J mol⁻¹ K⁻¹), \( k_B \) is the Boltzmann constant (J K⁻¹), \( T \) is the temperature in kelvin (K), h is Plank’s constant (J S), and \( R \) is the universal gas constant (J/mol K).

3. Results and discussion

3.1. XRD analysis

The XRD patterns indicate the impact of various ZnO concentrations and calcination temperatures on the crystal phase and crystallite size of SZ, as revealed in Figs. 1 and 2. The peaks at 2θ = 28.16° and 31.44° are characteristic of the monoclinic phase, while the peak at 2θ = 30.15° refers to the tetragonal phase, which is the more catalytically active phase [56].

Fig. 1 shows that undoped SZ contains a major monoclinic phase in addition to the tetragonal phase. The tetragonal phase of SZ with 6% ZnO is more stable as a result of decreasing lattice spacing and zirconia particle size [57,58] in addition to the surface energy effects, which stabilize the tetragonal phase as the particle size decreases [59]. The small particles are stabilized in the tetragonal phase because their surface energy is much lower than that of the monoclinic phase, which slows transformation from the metastable phase to the monoclinic phase. Therefore, the stability of the tetragonal phase might be related to the introduction of phase stabilizers on the surface (such as the sulphate groups) or in the bulk (such as the cationic dopant) [60]. Here, tetragonal phase stabilization was caused by the introduction of 6% ZnO into the SZ. However, when the ZnO concentration was increased to more than 6%, the content of the tetragonal phase decreased while that of the monoclinic phase increased. This behaviour can be
attributed to the large concentration of ZnO, which increases randomness, disfavouring oxygen diffusion and destabilising the tetragonal phase [61].

Fig. 2 shows the 6% Zn/SZ catalysts calcined at 500, 600 and 800 °C. As revealed in Fig. 2, the catalyst is mainly amorphous at 500 °C, while the highest proportion of tetragonal phase is observed at 600 °C. Calcination at 800 °C causes a sharp decrease in the tetragonal phase accompanied by an increase in the particle size.

The crystallite size calculations indicate that the crystallite size of undoped SZ decreases with the addition of 6% ZnO. The ionic radius of the Zn$^{2+}$ ion (0.74 Å) is smaller than that of the Zr$^{4+}$ ion (0.84 Å). Therefore, replacing a larger ion Zr$^{4+}$ with a smaller one Zn$^{2+}$ decreases the lattice constants and changes the crystallite size. Thus, it can be concluded that the lattice disorder that occurs at ZnO concentrations above 6% may be due to the difference in the ionic radii of Zn$^{2+}$ and Zr$^{4+}$ ions. Tewari et al. reached a similar conclusion for Al-doped ZnO.

Table 1 – Chemical analysis of SZ catalysts with different ZnO contents.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Wt.% of ZnO calculated from EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ</td>
<td>—</td>
</tr>
<tr>
<td>4%ZnO/SZ</td>
<td>4.00%</td>
</tr>
<tr>
<td>6%ZnO/SZ</td>
<td>5.95%</td>
</tr>
<tr>
<td>10%ZnO/SZ</td>
<td>8.82%</td>
</tr>
</tbody>
</table>

They observed that 0.5% Al-doped ZnO affords a minimum crystallite size of 103 nm. However, the crystallite size in the doped catalysts did not vary in any regular pattern with the Al dopant concentration [62].

3.2. EDX analysis

Fig. 3 reveals the chemical composition of the SZ catalysts doped with different concentrations of ZnO. The results corroborated that Zr, O, S and Zn are present in the catalyst structure. Furthermore, they show that the weight percent of ZnO in the nanocatalysts is in good agreement with the calculated weight percent from the synthesis of the catalysts, as observed in Table 1.

3.3. Adsorbed pyridine-FT-IR spectroscopy

Analysing the IR spectra with pyridine adsorbed as a base onto the surface of solid acids is a widely applied technique for investigating the Brønsted and Lewis acidity of catalysts. The pyridine molecules adsorbed on Brønsted and Lewis acid sites have different vibrational bands because of the difference in their bonding [52]. Figs. 4 and 5 show the IR spectra if the investigated catalysts with adsorbed pyridine over the 2000–500 cm$^{-1}$ region. The ZnO/SZ catalysts show bands typical of adsorbed pyridine at approximately 1450 cm$^{-1}$, assigned to pyridine coordinated to electron-acceptor sites (i.e., Lewis acid sites), and 1609 cm$^{-1}$ and 1626 cm$^{-1}$, assigned to pyridinium ions (pyH$^+$) adsorbed on protonic acid sites (i.e., Brønsted acid sites). The band at approximately 1489 cm$^{-1}$ arises from the interaction of pyridine species with both Brønsted and Lewis acid sites [63,64]. The SZ catalyst exhibits a typical band attributable to Brønsted acid sites.

The percentages of Lewis and Brønsted acid sites were examined based on the integrated areas or the relative intensities of the characteristic bands of pyridine adsorbed on Lewis and/or Brønsted acid sites. The percentages of Lewis and Brønsted acid sites can be calculated using the following equations [65]:

\[
\text{Lewis\%} = \left(\frac{A_L}{A_L + A_B}\right) \times 100
\]

\[
\text{Brønsted\%} = \left(\frac{A_B}{A_L + A_B}\right) \times 100
\]

where $A_B$ is the intensity of the peak located in the range of 1609–1626 cm$^{-1}$, which is attributed to the pyridinium cation adsorbed on Brønsted acid sites, and $A_L$ is the intensity of the peak at 1450 cm$^{-1}$ from pyridine coordinated to Lewis acid sites.

The sample with 6%ZnO/SZ calcined at 600 °C showed the optimum Brønsted to Lewis acid site (B/L) ratio, as shown in Fig. 6. Further increasing the ZnO loading decreased the B/L.
Fig. 3 – EDX pattern of (a) SZ, (b) 4%ZnO/SZ, (c) 6%ZnO/SZ, and (d) 10%ZnO/SZ catalysts calcined at 600 °C.

Fig. 4 – FTIR spectra of pyridine adsorbed on (a) SZ, (b) 6%ZnO/SZ, (c) 8%ZnO/SZ, (d) 10%ZnO/SZ and (e) 20%ZnO/SZ catalysts.

Fig. 5 – FTIR spectra of pyridine adsorbed on 6%ZnO/SZ catalyst calcined at (a) 500 °C, (b) 600 °C and (c) 800 °C.

ratio, which may be attributable to the aggregation of ZnO decreasing the accessibility of Lewis and Brønsted acid sites to pyridine. Karim et al. found similar results with WO3 loaded on ZrO2 [66].
**Fig. 6** – Effect of ZnO content on the B/L ratio of ZnO/SZ catalyst calcined at 600 °C.

**Fig. 7** – Effect of calcination temperature on B/L ratio of 6%ZnO/SZ catalyst.

**Table 2 – Systematic variation of concentration of resorcinol and ethyl acetoacetate.**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinol [A] (mol)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Ethyl acetoacetate [B] (mol)</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Product (mol)</td>
<td>$4.63 \times 10^{-3}$</td>
<td>$6.31 \times 10^{-3}$</td>
<td>$3.26 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

and S—OH species may serve as Brønsted acid sites according to the following scheme:

$$^*—O—H + \text{pyr} \rightarrow ^*—O— + ^*—H—\text{pyr}$$

(*” referstoeitherSorZr)

However, S—OH is a stronger Brønsted acid site. Therefore, losses of S—OH decrease the number of Brønsted acid sites [64,65].

### 3.4. Kinetic study

The Pechmann reaction has been intensely studied over different catalysts; however, the order, rate constants, and activation energy were not experimentally determined as discussed in this research. Based on density functional theory with the M06-2X functional, Pornsatitworakul et al. studied the preparation of 7-hydroxy-4-methyl coumarin. The authors claimed that theoretically the transesterification was the rate-determining step, and it had an overall activation energy of 40.0 kJ mol$^{-1}$. They suggested the theoretical pathway of 7-hydroxy-4-methyl coumarin synthesis as shown in **Fig. 8**; [AD (activated complex), IN (intermediate), TS (transition state), PR (product)] [39].

#### 3.4.1. Order of the reaction

For a chemical reaction, the order can be determined using the initial rate method or by using a program for data analysis. However, in reactions involving multiple reactants, the order of the reaction can be determined by varying the concentration of the reactants in a systematic way, as observed in **Table 2**, so that the order can be measured with respect to concentration change of one of the reactants by using the following rate equation:

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k_1 [A]_1^n [B]_1^m}{k_2 [B]_2^n [B]_2^m}$$

(3)

Where 1 and 2 refer to the experiment number, $k$ is the rate constant, $A$ is the concentration of resorcinol, $B$ is the concentration of ethyl acetoacetate, the exponent $\alpha$ is the order of the reaction with respect to $A$ and the exponent $\beta$ is the order of the reaction with respect to $B$. Then, the total reaction order can be given by the sum of exponents $\alpha$ and $\beta$.

**Table 2** shows the systematic variations in the concentrations of resorcinol and ethyl acetoacetate, and the results showed first-order reaction kinetics.

#### 3.4.2. Apparent activation energy

The reaction was performed over temperatures ranging from 353 to 393 K as observed in **Fig. 9**. The increase in the conversion of reactants by increasing the reaction temperature
indicates that the investigated reaction is kinetically controlled [69].

The rate constants were calculated at different temperatures and plotted as a function of 1/T as shown in Fig. 9 according to the Arrhenius equation:

$$\ln K = \ln A - E_a / R \cdot 1/T$$

(4)

Where k is the rate constant, $E_a$ is the activation energy, R is the gas constant, and A is the preexponential constant.

The value of $E_a$ was calculated to be 42.29 kJ mol$^{-1}$. This value is comparable to the theoretical value calculated by Pornsatitworakul et al. (40.0 kJ mol$^{-1}$). Thus, transesterification is the rate-determining step.

3.4.3. Activation enthalpy, entropy and free energy

The Eyring-Polanyi equation is used in chemical kinetics to describe variations in the rate of a chemical reaction with temperature. This equation is based on transition state theory.

The linear form of the Eyring-Polanyi equation is given as follows:

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R}$$

(5)

where $k$ is the rate constant, $T$ is the temperature in kelvin (K), $\Delta H^\ddagger$ is the activation enthalpy (kJ mol$^{-1}$), $\Delta S^\ddagger$ is the activation entropy (J mol$^{-1}$ K$^{-1}$), $k_B$ is the Boltzmann constant (J K$^{-1}$), $h$ is Plank’s constant (J/s), and $R$ is the universal gas constant (J/mol K).

The activation enthalpy and activation entropy were calculated from the slope and intercept of the straight line of Fig. 10. The values of $\Delta S^\ddagger$ and $\Delta H^\ddagger$ were used to calculate the free energy of activation using the following equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

(6)

Where $\Delta G^\ddagger$ is the free energy of activation (kJ mol$^{-1}$).

The results summarized in Table 3 show that the transesterification step had apparent activation energy of 42.29 kJ mol$^{-1}$, making this step endothermic by 39.20 kJ mol$^{-1}$. The negative value of $\Delta S^\ddagger$ reveals that the entropy decreases upon forming the transition state, which indicates that the transition state is more highly ordered than the reactants.

4. Conclusion

ZnO/SZ nanoparticles have been synthesized by a simple impregnation method. The results showed that SZ has a major monoclinic phase in addition to a tetragonal phase. The incorporation of ZnO increases the stability of the tetragonal phase as a result of decreasing the lattice spacing and particle size of zirconia. Increasing the ZnO concentration to more than 6 wt% led to decreasing the stability by decreasing the proportion of tetragonal phase with a concomitant increase in the mono-
Table 3 – Activation energy, activation enthalpy, entropy and free energy values for the investigated pechmann condensation reaction.

<table>
<thead>
<tr>
<th></th>
<th>E_r (kJ mol⁻¹)</th>
<th>ΔH° (kJ mol⁻¹)</th>
<th>ΔS° (J mol⁻¹ K⁻¹)</th>
<th>ΔG° (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>373 K</td>
<td>42.29</td>
<td>39.20</td>
<td>−152.62</td>
<td>96.13</td>
</tr>
<tr>
<td>383 K</td>
<td>42.29</td>
<td>39.20</td>
<td>−152.62</td>
<td>97.66</td>
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<tr>
<td>393 K</td>
<td>42.29</td>
<td>39.20</td>
<td>−152.62</td>
<td>99.18</td>
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</table>

Conflict of interest

The authors declare no conflicts of interest.

References
