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Article

Coke-tolerant SiW₂₀-Al/Zr₁₀ catalyst for glycerol dehydration to acrolein

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ABSTRACT

Glycerol dehydration to acrolein over a series of supported silicotungstic acid catalysts (SiW_x-Al/Zr_y) was investigated. Characterization results showed that the final catalyst had high thermal stability, a large pore diameter, strong Lewis acidic sites, and a large specific surface area. X-ray photoelectron survey spectra clearly showed peaks attributable to W (W 4f = 35.8 eV), Al₂O₃ (Al 2p = 74.9 eV), and ZrO₂ (Zr 3d = 182.8 eV). The highest acrolein selectivity achieved was 87.3% at 97% glycerol conversion over the SiW₂₀-Al/Zr₁₀ catalyst. The prepared catalysts were highly active and selective for acrolein formation even after 40 h because of the presence of high concentrations of Lewis acidic sites, which significantly reduced the amount of coke on the catalyst surface. Response surface methodology optimization showed that 87.7% acrolein selectivity at 97.0% glycerol conversion could be obtained under the following optimal reaction conditions: 0.5 wt% catalyst, reaction temperature 300 °C, and feed glycerol concentration 10 wt%. Evaluation of a mass-transfer-limited regime showed the absence of internal and external diffusions over pellets of diameter $d_p < 20 \mu\text{m}$. These results show that glycerol dehydration over a strong Lewis acid catalyst is a promising method for acrolein production.

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1. Introduction

The demand for green and clean energy has increased greatly because of significant CO₂ emissions and the depletion of fossil fuel resources. Intensive efforts have therefore been made by many researchers to produce value-added chemicals through biobased processes instead of conventional petroleum-based processes [1–3]. Biofuels such as biodiesel and ethanol are being used as substitutes for fossil fuels. Glycerol is the main byproduct of the biodiesel process, accounting for almost 10 wt% of the total products [4]. Some researchers have reported that over 41.9 billion liters of glycerol will be produced annually by 2020 [5]. The high availability of glycerol has significantly decreased its price from 1.2 \$/kg in 2001 to 0.4 \$/kg

in 2016 [5].

Glycerol is one of the top 12 most important biobased chemicals in the world because of its important characteristics such as non-toxicity, biosustainability, biodegradability, and edibility, together with its multi-functional structure (three hydroxyl groups) [6–8]. The physicochemical properties of glycerol make it suitable for various reactions, including dehydration, reforming, oxidation, hydrogenolysis, etherification, and esterification, for the synthesis of more than 2000 value-added chemicals or products [9,10]. Dehydration of glycerol to acrolein has attracted considerable attention as a renewable-based alternative to the conventional petroleum-based process, i.e., oxidation of propylene [11,12]. Acrolein is a versatile intermediate for the production of monomers such as

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acrylic acid, methionine, and super-absorbent polymers. These monomers are important in the production of polyesters and other polymers. The production of acrolein by the biobased glycerol dehydration route has not yet been commercialized, but the surge in the cost ratio of acrolein to glycerol has recently made the biobased process commercially viable [8,13].

In previous studies, various solid acid catalysts such as heteropoly acids (HPAs) [14–16], zeolites [17–19], and metal oxides [20,21], in gas or liquid [22] phases, have been used for glycerol dehydration to acrolein. However, the main drawback of solid acid catalysts in this field is coke deposition, which substantially decreases the catalytic activity. For example, a Cs-HPW catalyst gave the highest ever reported acrolein selectivity, namely 98%, at 100% glycerol conversion. However, the catalyst had poor stability and glycerol conversion decreased by 40% after just 6 h because of coke deposition on the catalyst surface [24,25]. The development of highly coke-tolerant catalysts for glycerol dehydration is therefore important. The large-scale biobased production of acrolein depends on overcoming the problem of fast catalyst deactivation. Small pore diameters, high reaction temperatures, low surface acidities, and strong Brønsted acidic sites on the catalyst surface are known to aggravate coke formation [26].

Co-feeding of hydrogen or oxygen was one of the first methods investigated for eliminating or slowing down coke deposition on catalyst surfaces [27]. However, this method can increase the possibility of explosive conditions or oxidation of products, which reduces the acrolein selectivity.

HPAs are widely used in the production of acrolein because of their strong acidities (Brønsted acidic sites) and high activities [28]. HPAs are environmentally friendly and reusable or recoverable in various reactions. These catalysts can also be used in continuous processes. The main disadvantages of HPAs are their small surface areas (1–10 m²/g) and low thermal stabilities. HPAs are therefore usually supported on carriers such as Al₂O₃, ZrO₂, and SiO₂ to overcome these limitations. A suitable pore structure, high surface acidity, and appropriate type of acidic sites (Brønsted or Lewis) are some of the criteria for enhancing catalytic activity [29–31]. Haider et al. [32] used noble metals (Rb and Cs) as the third component of the catalyst to enhance its stability and activity in glycerol dehydration to acrolein. They reported that the main reason for the higher activity and stability of the catalyst, even without gas co-feeding, was the use of Cs or Rb because large metal cations increase the interstitial volume between Keggin anions and the newly formed pores, and surface areas blocked by plugging can be renewed. However, noble metals are expensive and significantly increase production costs.

Recently, large pore diameters and Lewis acidic sites were reported to reduce coke deposition considerably in a process without gas co-feeding or loading the catalyst with noble metals [1,17,33–34]. The electronic interactions between the support and active phase can be either strong (e.g., with ZrO₂ or Al₂O₃) or weak (e.g., with SiO₂) and this strength affects the nature of the acidic sites and the thermal stability of the support. Strong interactions lead to distortion of the Keggin structure, which decreases the acid strength. Consequently, less coke

is formed because of the increased number of Lewis acidic sites.

In this study, a novel catalyst preparation procedure involving an active HPA component (HSiW) supported on γ -Al₂O₃ nanoparticles (NPs) and grafting the supported sample with ZrO₂ was investigated. It was envisaged that the γ -Al₂O₃ NPs could be used to tune the acidity and significantly enhance the amount of Lewis acidic sites, and provide a catalyst with a larger specific surface area and pore diameter compared with those of bulk HSiW. ZrO₂ was added to reduce catalyst deactivation and improve the life-time stability of the catalyst in the gas-phase dehydration of glycerol to acrolein. After the best catalyst with the highest selectivity for acrolein had been identified, response surface methodology (RSM) was used to determine the optimal values of the reaction parameters. The presence of internal and external diffusion at various feed flow rates (m_g), pellet diameters (d_p), and catalytic bed volumes (V_{cat}) was investigated to evaluate the catalyst efficiency during the reaction.

2. Experimental

Glycerol (purity >99%), HSiW, γ -Al₂O₃ NPs (<50 nm), ZrO₂, acetic acid, allyl alcohol, hydroxyacetone, acetone, propionaldehyde, and acetaldehyde (reagent grade) were supplied by Sigma Aldrich (Malaysia). Reagent-grade acrolein was purchased from Scientific Trends (M) Sdn. Bhd.

2.1. Catalyst preparation

First, a series of catalysts with different HSiW loadings (10, 20, 30, and 40 wt%) impregnated on γ -Al₂O₃ NPs were prepared. In detail, aqueous HSiW solutions (10 mL of water per gram of HSiW) were added drop-wise to the γ -Al₂O₃ support. The suspension was vigorously stirred for 12 h, followed by drying at 110 °C for 18 h. The HSiW-Al₂O₃ supported catalysts are denoted by SiW_x-Al (SiW₁₀-Al, SiW₂₀-Al, SiW₃₀-Al, and SiW₄₀-Al), where x is the weight percentage of HSiW supported on the γ -Al₂O₃.

A second series of catalysts were prepared by impregnation of ZrO₂ at different weight percentages (10–30 wt%) on the SiW₂₀-Al catalyst. In detail, ZrO₂ was mixed with water (10 mL of water per gram of ZrO₂) and the slurry was stirred continuously. An aqueous solution of SiW₂₀-Al was then added drop-wise to the ZrO₂ slurry. The mixture was stirred continuously for 20 h followed by drying at 120 °C for 18 h. These catalysts are denoted by SiW₂₀-Al/Zr_y (SiW₂₀-Al/Zr₁₀, SiW₂₀-Al/Zr₂₀, and SiW₂₀-Al/Zr₃₀), where y is the weight percentage of ZrO₂ supported on the SiW₂₀-Al sample. An Al₈₀-Zr₂₀ sample was similarly prepared by impregnation, but without HSiW, to evaluate the effect of the combination of γ -Al₂O₃ and ZrO₂ on the catalytic activity.

2.2. Catalyst characterization

The specific surface area, pore volume, and average pore diameter of catalyst were determined based on N₂ adsorp-

tion-desorption properties at $-196\text{ }^{\circ}\text{C}$ (SURFAR, Thermo Scientific). The average pore diameter was calculated using the Barrett-Joyner-Halenda method. The total acidities of the prepared catalysts were calculated using temperature-programmed desorption of NH_3 (NH_3 -TPD; Auto Chem II, Micromeritics). A specific amount of catalyst was dried at $200\text{ }^{\circ}\text{C}$ for 1 h and saturated with NH_3 at $60\text{ }^{\circ}\text{C}$ for 0.5 h, and then the physically adsorbed NH_3 was removed by He purging at $60\text{ }^{\circ}\text{C}$ for 0.5 h. The temperature was ramped to $700\text{ }^{\circ}\text{C}$ at a heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$ to desorb the chemically adsorbed NH_3 .

Pyridine adsorption infrared (Py-IR) spectroscopy was performed on the prepared catalysts using a 170-SX FTIR spectrophotometer to determine the nature of the acidic sites (Brönsted and Lewis). Powdered samples (50 mg) were pressed ($5\text{ ton}/\text{cm}^2$) into thin pellets of diameter approximately 20 mm for the pyridine adsorption tests. The prepared pellets were pretreated in a high-vacuum system at $300\text{ }^{\circ}\text{C}$ and 0.013 Pa overnight. The samples were cooled to room temperature under vacuum and liquid pyridine ($2\text{ }\mu\text{L}$) was injected into the system. Spectra were recorded at 150 and $250\text{ }^{\circ}\text{C}$ after evacuation for 60 min.

X-ray diffraction (XRD) was used to determine the structures of the prepared catalysts, and to evaluate their degrees of crystallinity. The XRD patterns were obtained with a D5000 Siemens instrument using $\text{Cu K}\alpha$ radiation (40 kV , 40 mA). The patterns were recorded in the 2θ range 10° – 80° (step width 0.05° , 1 s per step). X-ray photoelectron spectroscopy (XPS) was performed using an Omicron DAR 400 analyzer. The samples were fixed to the sample holder using carbon tape. The pass energy used was 20 eV , and the instrument was operated at 15 kV . The spectra were recorded in the range 0 – 1200 eV , and the binding energies were calibrated against the $\text{C } 1\text{s}$ signal (284.6 eV) as an internal standard. Thermogravimetric analysis (TGA) was performed using a Thermo TGA instrument in the temperature range 30 – $800\text{ }^{\circ}\text{C}$, with a ramping rate of $10\text{ }^{\circ}\text{C}/\text{min}$, under a N_2 flow. The sample morphologies were examined using field-emission scanning electron microscopy (FESEM; SU-8000, Hitachi, with a STEM detector) and transmission electron microscopy (TEM; FEI-Tecni G2) at 300 kV . The coke content of the used catalyst was determined using a Thermo Scientific Flash 2000 instrument.

2.3. Catalytic activity tests

The gas-phase dehydration of glycerol was performed at atmospheric pressure in a vertical fixed-bed Pyrex reactor (30 cm length, 11 mm i.d.) using the catalyst (1 g , $d_p = 0.5$ – $5\text{ }\mu\text{m}$) sandwiched between plugs of glass wool. Prior to the reaction, the catalyst was pretreated at the reaction temperature ($300\text{ }^{\circ}\text{C}$) in a N_2 flow for 1.5 h. Aqueous glycerol ($10\text{ wt}\%$) was preheated to $300\text{ }^{\circ}\text{C}$ to ensure complete vaporization and then swept into the reactor, using a syringe pump, at a $2\text{ mL}/\text{h}$ flow rate. The gas hourly speed velocity (GHSV) of the inert carrier gas was 1200 h^{-1} . The products and unconverted glycerol were condensed and collected hourly for analysis. *n*-Butanol was added to the condensed products as an internal standard. The final solution was analyzed using a gas chromatography system

equipped with capillary column (DB-Wax; $30\text{ m} \times 0.53\text{ mm} \times 0.25\text{ }\mu\text{m}$) and a flame ionization detector. The column was held at $40\text{ }^{\circ}\text{C}$ for 4 min and then the temperature was ramped up to $200\text{ }^{\circ}\text{C}$ at a rate of $12\text{ }^{\circ}\text{C}/\text{min}$ and held for 23 min to achieve effective product separation. The glycerol conversion, product yields, selectivities, and carbon balance are defined by Eqs. (1) to (4):

$$\text{Conv}_{\text{Gl}}(\%) = (M_{\text{Gl, in feed}} - M_{\text{Gl, in outlet}} / M_{\text{Gl, in feed}}) \times 100\% \quad (1)$$

$$\text{Sel}_{\text{N}}(\%) = (M_{\text{C in product, N}} / M_{\text{C in Gl, feed}} - M_{\text{C in Gl, outlet}}) \times 100\% \quad (2)$$

$$\text{Yield}_{\text{N}}(\%) = \text{Conv}_{\text{Gl}}(\%) \times \text{Sel}_{\text{N}}(\%) \quad (3)$$

Carbon balance = sum of the selectivities of identified products (4) where M_{Gl} and M_{C} are moles of glycerol and carbon for each product (N).

2.4. Experimental design

Five-level three-factor central composite design, which required 20 experimental runs, was used in this study. The ranges and the design levels for each variable are summarized in Table 1. The performance of the optimization process was evaluated by analyzing the acrolein selectivity as the response. The quadratic equation for optimization is

$$\eta = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^3 \beta_{ij} X_i X_j + \varepsilon \quad (5)$$

where η is the response; β_0 is a constant coefficient; β_i , β_{ii} , and β_{ij} are linear, quadratic, and second-order interaction coefficients, respectively; X_i and X_j are independent variables; and ε is the error. Design Expert (6.0.7, State Ease, Inc., USA) was used for regression (analysis of variance) analysis.

3. Results and discussion

3.1. Surface area and porosity determination

The textural characteristics of the supported HSiW catalysts are summarized in Table 2. The results show that increasing the HSiW loading on $\gamma\text{-Al}_2\text{O}_3$ from $10\text{ wt}\%$ to $40\text{ wt}\%$ decreased the catalytic specific surface area from 140.5 to $76.6\text{ m}^2/\text{g}$. Because of the non-porous nature of HSiW, the reduction in the surface area was proportional to the amount of deposited active phase. The pore volume decreased from 0.5 to $0.2\text{ cm}^3/\text{g}$ from pure $\gamma\text{-Al}_2\text{O}_3$ to $\text{SiW}_{40}\text{-Al}$. The highest HSiW loading reduced the pore volume (V_p) by approximately 50% . However, the average pore diameter remained constant at about 21 nm .

Impregnation of $10\text{ wt}\%$ to $30\text{ wt}\%$ ZrO_2 on the $\text{SiW}_{20}\text{-Al}$ sample slightly decreased the surface area from 96.9 to $77.3\text{ m}^2/\text{g}$ and the pore volume decreased from 0.4 to $0.3\text{ cm}^3/\text{g}$. The Brunauer-Emmet-Teller surface area (A_{BET}) and V_p decreased because of plugging of the micropores [17]. The average pore diameter was about 1 – 2 nm less than that for the first series of

Table 1

Experimental level coding and range of independent variables.

Independent parameters	Code	Coded levels of parameters				
		$-\alpha$	-1	0	$+1$	$+\alpha$
Temperature ($^{\circ}\text{C}$)	A	270	285	300	315	330
Catalyst (wt%)	B	0.1	0.3	0.5	0.7	0.9
Glycerol feed (wt%)	C	0.5	5	10	15	20

Table 2

Bulk and supported catalyst surface areas (A_{BET}), pore volumes (V_p), and pore diameters (D_p).

Catalyst	A_{BET} (m ² /g)	V_p (cm ³ /g)	D_p (nm)
HSiW	8.2	0.02	10.3
ZrO ₂	14.0	0.06	37.0
γ -Al ₂ O ₃	143.2	0.5	22.5
Al ₈₀ -Zr ₂₀	118.0	0.6	19.6
SiW ₁₀ -Al	140.5	0.4	21.0
SiW ₂₀ -Al	125.7	0.4	21.5
SiW ₃₀ -Al	115.7	0.4	21.1
SiW ₄₀ -Al	76.6	0.2	21.6
SiW ₂₀ -Al/Zr ₁₀	96.9	0.4	19.1
	(93.0) ^a	(0.4) ^a	(18.2) ^a
SiW ₂₀ -Al/Zr ₂₀	90.0	0.3	19.4
SiW ₂₀ -Al/Zr ₃₀	77.3	0.3	20.5

^a Spent catalyst surface area, pore volume, and average pore diameter.

catalysts, and remained constant at 19–20 nm for the final series of samples. The results (not shown here) suggest that for the majority of pores, the diameter, D_p , was less than 6 nm (radius less than 8 nm).

The A_{BET} , V_p , and D_p values for the spent SiW₂₀-Al/Zr₁₀ catalyst are also shown in Table 2. The results show that the spent catalyst still had high activity after reaction for 12 h. The spe-

cific surface area (93.0 m²/g) decreased by less than 4% and the pore diameter and pore volume remained almost constant, indicating long-term catalytic activity.

3.2. Catalyst acidity determination

The NH₃-TPD profiles and acid strengths of the prepared catalysts are shown in Fig. 1 and listed in Table 3. HSiW and Al₈₀-Zr₂₀ had the highest acidities. The main difference between these two samples is their acid strengths. HSiW has 20 and 1600 $\mu\text{mol/g}$ of weak and strong acidic sites, respectively, whereas Al₈₀-Zr₂₀ has 700 and 1000 $\mu\text{mol/g}$ of weak and medium-strength acidic sites, respectively. The acidity of the supported HSiW catalysts increased significantly, from 2000 to 2600 $\mu\text{mol/g}$, with increasing HSiW loading (10 wt% to 40 wt%) on γ -Al₂O₃. All the samples show two peaks, at 132–138 and 301–318 °C, corresponding to weak and medium acid strengths. The shift in the peak position in Fig. 1(a) confirms that the acid strength increased with increasing HSiW from 10 wt% to 40 wt%. The main reason for the shift is electronic interactions between HSiW and γ -Al₂O₃. During impregnation, the hydroxyl groups on the surface of γ -Al₂O₃ are protonated, giving a positively charged surface. The strong electronic in-

Fig. 1. NH₃-TPD profiles of supported (SiW_x-Al) (a) and supported (SiW_x-Al/Zr_y) (b) samples.

Table 3

NH₃-TPD acidities of bulk and supported HSiW catalysts.

Catalyst	Weak ^a		Medium ^b		Strong ^c		Total acidity ^e
	Tem. (°C) ^d	Acidity ^e	Tem. (°C) ^d	Acidity ^e	Tem. (°C) ^d	Acidity ^e	
HSiW	132; 251	20	—	—	546	1600	1620
ZrO ₂	127; 280	100	415	100	—	—	200
γ -Al ₂ O ₃	127; 288	1200	—	—	—	—	1200
Al ₈₀ -Zr ₂₀	130; 300	700	365; 440	1000	—	—	1700
SiW ₁₀ -Al	132	1000	301	1000	—	—	2000
SiW ₂₀ -Al	138	500	302	1800	—	—	2300
SiW ₃₀ -Al	136	500	311	2000	—	—	2500
SiW ₄₀ -Al	136	600	318	2000	—	—	2600
SiW ₂₀ -Al/Zr ₁₀	138	1600	304	1000	—	—	2600
SiW ₂₀ -Al/Zr ₂₀	139	2000	308	1400	—	—	3400
SiW ₂₀ -Al/Zr ₃₀	139	2100	313	1600	—	—	3700

^a Weak (150 to $\leq$ 300 °C). ^b Medium (300–450 °C). ^c Strong ($\geq$ 450 °C). ^d NH₃ peak position (°C). ^e Acid amount ($\mu\text{mol/g}$).

teractions stabilize the Keggin structure, which significantly enhances the thermal stabilities of the supported catalysts [17].

The total acidity of the supported $\text{SiW}_{20}\text{-Al/Zr}_{10-30}$ catalysts increased from 2600 to 3700 $\mu\text{mol/g}$ with increasing ZrO_2 loading to 30 wt%. Fig. 1(b) clearly shows that impregnation with ZrO_2 did not change the peak position, indicating no improvement in the acid strength. The acidity results clearly distinguish the two series of supported samples. The $\text{SiW}_x\text{-Al}$ samples have higher amounts of medium-strength acidic sites than of weak acidic sites. However, the final series of catalysts ($\text{SiW}_{20}\text{-Al/Zr}_y$) clearly have higher amounts of weak acidic sites than of medium ones.

The acidic nature significantly affects the catalytic activity. FTIR pyridine tests were performed to determine the amounts of Brönsted and Lewis acidic sites on each catalyst. Fig. 2 shows the standard pyridine adsorption spectra (nature of acidity) for the final series of catalysts ($\text{SiW}_{20}\text{-Al/Zr}_y$) at 150 °C. The spectra show bands at approximately 1445, 1490, and 1540 cm^{-1} for Lewis, combined Brönsted-Lewis, and Brönsted acidic sites, respectively [35]. The concentrations of Brönsted and Lewis acidic sites in the samples are 22.627.8 and 37.5–44.3 $\mu\text{mol/g}$, respectively, as shown by the peaks at 1540 and 1445 cm^{-1} , respectively (Table 4). The presence of a large amount of Lewis acidic sites in HPA catalysts supported on Al_2O_3 is in good agreement with previous reports [26,36–38]. The NH_3 -TPD and FTIR pyridine results clearly confirm our initial hypothesis that the use of $\gamma\text{-Al}_2\text{O}_3$ as a support could be used to tune the acidity and increase the amount of Lewis acidic sites in the supported sample.

3.3. Structural analysis

The XRD patterns of the catalysts are shown in Fig. 3. The HSiW shows diffraction peaks at 10.9°, 25.5°, and 34.7°, corresponding to Keggin anions [39]. The diffraction peaks associated with bulk $\gamma\text{-Al}_2\text{O}_3$ appear at 18.75°, 36.9°, 44.2°, and 67.3°. However, $\text{SiW}_{20}\text{-Al}$ does not show peaks from HSiW Keggin structures because of the high dispersion of 20 wt% HSiW on

Table 4

Concentrations of Brönsted and Lewis acidic sites.

Catalyst	Concentration of LAS ^a ($\mu\text{mol/g}$)	Concentration BAS ^a ($\mu\text{mol/g}$)	B/L ^b
$\text{SiW}_{20}\text{-Al/Zr}_{10}$	37.5	22.6	0.60
$\text{SiW}_{20}\text{-Al/Zr}_{20}$	38.3	24.1	0.63
$\text{SiW}_{20}\text{-Al/Zr}_{30}$	44.3	27.8	0.63

^a Concentrations of Lewis acidic sites (LAS) and Brönsted acidic sites (BAS) determined from the intensities of the IR bands at 1445 and 1540 cm^{-1} for adsorbed pyridine using Emeis' method [26,32].

^b Ratio of Brönsted to Lewis acidic sites.

$\gamma\text{-Al}_2\text{O}_3$ NPs, small size of Keggin anions ($D = 1.2$ nm), and large surface area of the support ($A_{\text{BET}} = 143.2$ m^2/g). A high concentration of HSiW is required to saturate the support surface. Atia et al. [26] reported that HSiW loadings greater than 80 wt% could saturate the $\gamma\text{-Al}_2\text{O}_3$ surface and could be detected by XRD. When the ZrO_2 loading on the supported catalyst was increased, the main ZrO_2 peaks, at 28.2° and 31.5°, were observed. The magnitudes of the ZrO_2 diffraction peaks increased, whereas those of $\gamma\text{-Al}_2\text{O}_3$, at 18.75°, 44.2°, and 67.3°, decreased.

3.4. Surface chemical states

The chemical states of the supported catalyst $\text{SiW}_{20}\text{-Al/Zr}_{10}$ were investigated using XPS. As shown in Fig. 4(a), peaks attributed to Al_2O_3 (Al 2p = 74.9 eV), ZrO_2 (Zr 3d = 182.8 eV), W (W 4f = 35.8 eV), oxygen (O 1s = 530.6 eV), and carbon (C 1s = 284.6 eV) are clearly observed in the survey spectrum.

The binding energy of W 4f appears as two peaks, at 35.8 and 37.8 eV (Fig. 4(b)). The peak at 35.8 eV is assigned to W^{6+} [40]. Unlike XRD (Fig. 3), which did not detect HSiW in the synthesized catalysts, XPS clearly confirms the presence of HSiW on the catalyst surface. The Al 2p spectrum shows a peak at 74.9 eV (Fig. 4(c)). The Al 2p peak for pure Al_2O_3 is observed at 74.7 eV [41]. The slight shift in the position of the Al 2p binding energy for the synthesized sample suggests that

Fig. 2. Standard FTIR spectra of pyridine adsorbed on synthesized catalysts at 150 °C.

Fig. 3. XRD patterns of pure and supported catalysts. (1) HSiW; (2) Al_2O_3 ; (3) $\text{SiW}_{20}\text{-Al}$; (4) ZrO_2 ; (5) $\text{SiW}_{20}\text{-Al/Zr}_{10}$; (6) $\text{SiW}_{20}\text{-Al/Zr}_{20}$; (7) $\text{SiW}_{20}\text{-Al/Zr}_{30}$.

Fig. 4. XPS spectra of SiW₂₀-Al/Zr₁₀. (a) Survey spectrum; (b) W 4f; (c) Al 2p; (d) Zr 3d; (e) O 1s.

γ -Al₂O₃ strongly binds with ZrO₂ and HSiW. Fig. 4(d) shows that the binding energies of Zr 3d_{5/2} and Zr 3d_{3/2} are 182.9 and 185.3 eV, respectively. The O 1s spectrum shows a peak at 530.6 eV (Fig. 4(e)) corresponding to the oxygen in the W–O–W unit of the Keggin structure [40,42].

The binding energies and intensities of all the elements in the final group of catalysts (SiW₂₀-Al/Zr_y) are reported in Table 5. All the reported binding energies are similar and the slight shifts are related to the presence of more than one type of species with different chemical characteristics, and electron transfer between the promoter and the support [43].

3.5. Thermal stability

TGA-differential thermal analysis (DTA) was performed to evaluate the thermal stabilities of the prepared SiW₂₀-Al and SiW₂₀-Al/Zr₁₀ catalysts in a N₂ flow. Bulk HSiW shows three weight-loss steps; the first two weight losses, of 8% at 85 °C and 3% at 200 °C, correspond to the loss of physically adsorbed water and water removal from hydrated HSiW, respectively

[26,44]. The final weight loss (1%), at >500 °C, indicates decomposition of the HSiW Keggin anions (Fig. 5(a)) [45,46].

Fig. 5(b) shows the DTA curves for all the bulk and supported samples. The DTA curves of the supported SiW₂₀-Al and SiW₂₀-Al/Zr₁₀ catalysts show similar trends. The clear broad peak at 80 °C corresponds to the loss of physically adsorbed water, and the second weight loss, observed at 340 °C, is attributed to the removal of structural water molecules. The high thermal stabilities of the prepared samples are attributed to inherent electronic interactions between HSiW and the supports.

The TGA results for the spent and fresh SiW₂₀-Al/Zr₁₀ catalysts are shown in Fig. 5(c). The DTA curves of the fresh and used catalysts show similar peaks, at 80 and 340–400 °C. However, the spent sample gives an exothermic peak at 570 °C, but decomposition of the HSiW Keggin anions does not occur for the fresh catalyst, which is stable even above 570 °C. Katryniok et al. [17] reported that the decomposition of deposited carbonaceous species, formed during dehydration, was the main reason for the sample weight loss and the exothermic peak at 570 °C. The spent catalyst was therefore still stable at the reaction temperature (280–320 °C), even after 12 h, and coke deposited at 570 °C (significantly higher than the reaction temperature range) caused decomposition.

3.6. Morphological analysis

Table 5

Binding energies (eV) for final series of catalysts (SiW₂₀-Al/Zr_{10–30}).

Sample	W 4f	Al 2p	Zr 3d	O 1s
SiW ₂₀ -Al/Zr ₁₀	35.8	74.9	182.9	530.6
SiW ₂₀ -Al/Zr ₂₀	36.1	74.8	183.5	530.8
SiW ₂₀ -Al/Zr ₃₀	35.9	74.9	182.8	530.0

Fig. 5. (a) TG plots for bulk samples and supported HSiW catalysts; (b) DTA plots for all samples; (c) DTA plots for fresh and used SiW₂₀-Al/Zr₁₀ catalysts.

Fig. 6 shows the results for morphological analysis of fresh and used SiW₂₀-Al/Zr₁₀ catalysts. FESEM and TEM images of the fresh catalyst show that the large surface area (96.7 m²/g), pore volume (0.4 cm³/g), and uniform mesoporous structure of the support enable trapping of HSiW particles inside the pores (Figs. 6(a) and (b)) [47,48]. Figs. 6(c) and (d) show that the surface morphology of the spent catalyst does not differ from that of the fresh catalyst. The FESEM images confirm that the morphological properties of the catalyst remain unchanged because of the high hydrothermal stability of nano γ -Al₂O₃. Similar results have been reported elsewhere [35,49,50]. Figs. 6(c) and (d) clearly show that the used catalyst has a large surface area and high porosity, indicating that deposited coke only partially fills the pores on the catalyst surface. This is attributed to the large pore diameter (19–21 nm), and the catalyst remained stable even after a prolonged reaction time.

The energy-dispersive X-ray spectroscopy (EDX) results for the fresh SiW₂₀-Al/Zr₁₀ catalyst are shown in Figs. 6(e)–(h). EDX mapping confirms that Al₂O₃ (Fig. 6(e)), W (Fig. 6(f)), and ZrO₂ (Fig. 6(g)) are uniformly distributed throughout the prepared catalysts. EDX analysis (Fig. 6(h)) also shows that the amounts of Al, W, Si, and Zr in the catalyst are 64.9, 16.2, 9.6, and 9.5 wt%, similar to the theoretical values of 70 wt%, 20 wt%, and 10 wt% for γ -Al₂O₃, HSiW, and ZrO₂, respectively.

The TEM micrographs of the fresh SiW₂₀-Al/Zr₁₀ catalyst in Figs. 6(i) and (j) indicate that HSiW is well dispersed with regularly shaped particles. The high dispersion and dark micelles of HSiW on the support, shown by TEM, are in agreement with the XRD results. HPAs consist of heavy metals, and the TEM results clearly indicate strong electron scattering [50]. The HSiW particle size is in the range 20–40 nm (Fig. 6(j)).

3.7. Catalytic activity results

All catalytic measurements were made in the kinetically limited region. First, the gas-phase catalytic dehydration of glycerol to acrolein was investigated over SiW_x-Al catalysts at various temperatures between 280 and 320 °C for 3 h (Table 6). Increasing the HSiW loading from 10 to 20 wt% increased the acrolein selectivity. Well-dispersed HSiW on the γ -Al₂O₃ NP surfaces improves glycerol molecule access to the catalytically active protons on the support and consequently increases the

glycerol conversion [26]. However, when the HSiW loading was increased beyond 20 wt%, the number of active sites on

Fig. 6. FESEM images of fresh supported SiW₂₀-Al/Zr₁₀ catalyst (a,b) and used SiW₂₀-Al/Zr₁₀ catalyst (c,d); EDX mapping analysis of fresh SiW₂₀-Al/Zr₁₀ catalyst: (e) Al, (f) W, (g) Zr, and (h) EDX mapping results; (i,j) TEM micrographs showing active component particle size and distribution in synthesized SiW₂₀-Al/Zr₁₀ catalyst.

Table 6Catalytic performances over bulk and supported (10–40 wt%) HSiW on nano-sized γ -Al₂O₃ in glycerol dehydration to acrolein.^a

Catalyst	Tem. (°C)	X (%)	Y ^b (%)	Selectivity (%)							
				AC ^c	Et ^d	Pr ^e	Act ^f	Ha ^g	Aa ^h	Aca ⁱ	CB ^j
Blank	300	56.0	11.6	20.7	—	—	3.8	23.0	—	18.3	67.7
γ -Al ₂ O ₃	300	80.0	27.0	33.7	0.2	0.2	3.8	7.6	2.7	1.2	55.6
ZrO ₂	300	80.0	24.7	30.9	0.1	0.1	4.2	16.4	2.2	24.9	79.8
Al ₈₀ -Zr ₂₀	300	88.0	32.9	37.4	2.2	1.8	6.4	12.6	2.5	25.0	89.0
HSiW	300	85.0	32.4	38.1	4.2	5.9	4.5	16.6	5.1	11.2	87.2
SiW ₁₀ -Al	280	89.0	50.6	56.8	6.9	5.5	4.5	12.5	1.5	3.8	93.5
	300	92.0	55.4	60.2	4.5	4.2	3.4	10.7	1.3	6.1	92.7
	320	93.0	50.8	54.6	8.7	3.3	3.9	14.1	1.9	6.3	93.9
SiW ₂₀ -Al	280	90.0	64.2	71.3	2.2	2.1	3.1	3.6	4.1	8.3	95.9
	300	94.0	69.7	74.1	1.1	1.1	2.4	3.3	5.8	5.3	94.6
	320	97.0	60.7	62.6	3.9	4.9	5.6	5.6	5.5	6.7	95.8
SiW ₃₀ -Al	280	87.0	53.2	61.1	4.9	3.6	5.3	7.9	4.1	5.8	94.9
	300	91.0	60.9	66.9	4.1	4.9	5.4	6.1	1.3	6.1	96.3
	320	93.0	55.6	59.7	5.2	5.9	4.8	6.2	8.5	4.8	97.8
SiW ₄₀ -Al	280	86.0	55.8	64.8	5.4	4.3	6.0	5.9	1.5	6.5	96.6
	300	88.0	56.3	64.0	5.2	5.2	4.4	7.9	1.8	6.4	95.8
	320	95.0	58.8	61.9	4.6	4.1	3.6	9.5	1.2	7.2	93.9

^a Reaction conditions: feed, 2 mL/h; 10 wt% aqueous glycerol solution; carrier gas flow rate, 20 mL/min; reaction temperature, 300 °C; time on stream, 3 h; 1 g of catalyst. ^b Acrolein yield. ^c Acrolein. ^d Ethanal. ^e Propanal. ^f Acetone. ^g Hydroxyacetone. ^h Allyl alcohol. ⁱ Acetic acid. ^j Carbon balance.

γ -Al₂O₃ and the acid strength became the dominant factors. Coke deposition on the catalyst surface therefore increased significantly and catalyst deactivation accelerated, as previously reported [27]. Glycerol conversion increased from 90.0% to 97.0% with increasing temperature from 280 to 320 °C over the SiW₂₀-Al catalyst; this is in good agreement with the results of previous studies [51]. The SiW₂₀-Al catalyst gave the best performance, with the highest acrolein selectivity, namely 74.1%, corresponding to 94.0% glycerol conversion, at 300 °C. The activity of SiW₂₀-Al was better (selectivity 74.1% with 94% conversion) than that of a 30 HZ sample, which we previously reported [33,34]. The γ -Al₂O₃ NP support significantly enhanced the catalytic activity of HSiW compared with a ZrO₂ support. The SiW₂₀-Al catalyst was therefore selected for further investigation.

The activities of the final series of catalysts at different temperatures are summarized in Table 7. The catalyst with 10 wt% ZrO₂ loading, SiW₂₀-Al/Zr₁₀, gave the highest acrolein selectivity, i.e., 87.3% with 97.0% glycerol conversion at 300 °C. The conversion increased with increasing temperature from 93.0% to 100%. The selectivities for the main byproducts were 3.0%, 2.2%, and 2.1% for acetic acid, acetone, and propionaldehyde, respectively. The selectivity for the stable byproduct hydroxyacetone was 0.4%; its production in previous studies has been reported [24,52]. Hydroxyacetone is either produced by protonation of a terminal hydroxyl group of glycerol or formed during the dehydration and deprotonation of the protonated intermediates [43,53]. Another important byproduct is acetaldehyde, which is formed by 3-hydroxypropanol and acrolein cracking [46,54]. A low catalyst total acidity favors acetaldehyde production. Oxidation of acetaldehyde produces acetic acid [55]. Generally, the carbon balances over supported samples were high (92.7%–99.4%). Bulk samples gave low

carbon balances, which indicates low activities and the production of undesired and/or unknown products. SiW₂₀-Al/Zr₁₀ was the best catalyst because it gave the highest acrolein selectivity, corresponding to the highest turnover frequency (TOF), i.e., 201 h⁻¹ at 300 °C. Details of TOF value calculations are reported in our previous paper [33].

The catalytic activity decreased with increasing ZrO₂ loading from 10 wt% to 30 wt%. Table 3 and Fig. 1 show that increasing the ZrO₂ loading from 10 to 30 wt% caused the total acidity to increase significantly from 2600 to 3700 μ mol/g; however, the absence of shifts in the peak positions in Fig. 1 suggest that the acid strength was unaffected. The numbers of weak acidic sites in the SiW₂₀-Al/Zr_y catalysts were lower than those of medium acidic sites, in agreement with the pyridine test results (Table 4). The relationship between the number of acidic sites and the catalytic activity was also investigated; the results show that the amount of acidic sites ($Total\ acidity\ (NH_3-TPD)/Surface\ area\ (BET)\ (mmol/m^2)$) increased from 26.8 to 47.9 μ mol/m² with increasing ZrO₂ loading from 10 wt% to 30 wt%. A smaller catalyst surface area (A_{BET}) and significant increase in acidity (NH₃-TPD) leads to a sharp increase in the number of acidic sites. The large increase in the number of acidic sites is in good agreement with the decreased catalytic activity caused by greater coke deposition on the catalyst surface and faster deactivation of the SiW₂₀-Al/Zr₂₀ and SiW₂₀-Al/Zr₃₀ catalysts compared with SiW₂₀-Al/Zr₁₀.

The Brönsted acid concentration/Lewis acid concentration ratio increased slightly with increasing ZrO₂ loading. The activity of the SiW₂₀-Al/Zr₁₀ catalyst, with a low Brönsted acid concentration/Lewis acid concentration ratio of 0.6, was higher than the activities of the others. The catalytic activity tests confirm that a catalyst with a lower amount of Brönsted acidic sites and larger amount of Lewis acidic sites is effective for the selec-

Table 7Catalytic performances over 10–30 wt% ZrO₂-supported SiW₂₀-Al catalyst in dehydration of glycerol to acrolein. ^a

Catalyst	Tem. (°C)	X (%)	Y ^a (%)	Selectivity (%)								TOF ^k (h ⁻¹)
				Ac ^c	Et ^d	Pr ^e	Act ^f	Ha ^g	Aa ^h	Aca ⁱ	CB ^j	
SiW ₂₀ -Al/Zr ₁₀	280	93.0	76.3	82.1	2.6	1.4	2.7	2.8	1.3	4.0	98.2	181
	300	97.0	84.6	87.3 [88.1] ^l	1.2	2.1	2.2	0.4	1.6	3.0	99.4	201
	320	100	83.2	83.2	2.1	1.6	2.1	1.6	2.1	3.3	97.7	197
SiW ₂₀ -Al/Zr ₂₀	280	90.0	71.2	79.1	1.6	1.5	2.6	4.2	4.6	2.7	98.4	169
	300	94.0	78.9	83.9 [86.3] ^l	1.1	0.8	0.9	1.2	6.3	3.3	97.9	187
	320	97.0	77.3	79.7	1.5	0.9	2.8	3.7	2.8	3.6	96.3	183
SiW ₂₀ -Al/Zr ₃₀	280	92.0	72.6	78.9	2.4	3.0	1.7	2.5	4.9	2.3	97.2	172
	300	93.0	75.5	81.2 [84.4] ^l	1.1	0.9	1.1	1.3	7.6	1.8	95.9	179
	320	98.0	76.9	78.5	1.3	2.2	2.0	3.2	5.2	1.6	96.0	182

^{a–j} see Table 6. ^k TOF values after reaction for 3 h. ^l Acrolein selectivity after 1 h.

tive conversion of glycerol to acrolein. The results also show that strong acidic sites (Lewis or Brönsted) have negative effects on the catalytic activity. All these findings are in good agreement with our initial hypothesis that γ -Al₂O₃ NPs could be used to tune the acidity, significantly enhance the amount of Lewis acidic sites, and provide a supported sample with a larger specific surface area and pore diameter compared with those of bulk HSiW.

The excellent catalytic activity of the SiW₂₀-Al/Zr₁₀ catalyst is attributed to its acidity and hydrolytic stability in an aqueous environment [56]. Furthermore, catalysts with large pore diameters (>19 nm) have high stability. A catalyst with a pore diameter greater than 4 nm is more effective because it provides the required space for Keggin anions ($D = 1.2$ nm) at the surface, and increases the interactions between adsorbed glycerol molecules and Keggin anions [9]. Moreover, a large pore diameter decreases the impact of internal mass transfer limitations [55].

Figs. 7(a)–(c) show the glycerol conversions and acrolein selectivities for the final series of catalysts (SiW₂₀-Al/Zr_{*y*}) for a reaction time of 12 h. The glycerol conversion and acrolein selectivity decreased with reaction time for all three samples. The glycerol conversion with SiW₂₀-Al/Zr₁₀, the most active sample, gradually decreased from 97.0% to 82.0%, and the acrolein selectivity decreased by 6%, from 88% to 82%, during the first 7.5 h and then remained constant at 81.2%. In contrast, Figs. 7(b) and (c) show significant reductions in the glycerol conversions and acrolein selectivities for the other two samples. SiW₂₀-Al/Zr₂₀ and SiW₂₀-Al/Zr₃₀ gave less than 65% acrolein selectivity at approximately 75% glycerol conversion. Fig. 7(d) shows the long-term stability of the SiW₂₀-Al/Zr₁₀ catalyst, i.e., during reaction for 40 h. The SiW₂₀-Al/Zr₁₀ sample, with more than 76.0% acrolein selectivity at 78.0% glycerol conversion, retained its activity for up to 40 h.

3.8. Coke deposition

Table 8 summarizes the coke contents of the spent catalysts at various temperatures. Increasing the HSiW loading on γ -Al₂O₃ from 10 wt% to 40 wt% increased the coke content from 2.8 wt% to 4.7 wt% within 3 h at 300 °C; this is similar to previously reported results [27]. In addition, a higher reaction

temperature (320 °C) further increased coke deposition on the catalyst surface. Coke deposition over the SiW₂₀-Al and SiW₄₀-Al samples increased with increasing reaction temperature. The SiW₄₀-Al sample had the highest carbon content, namely 7.6 wt% at 320 °C.

Evidently, the higher total number of weak acidic sites in the final series of catalysts decreased the coke content. In the final series of catalysts, SiW₂₀-Al/Zr₁₀ gave coke deposition of only 1.3 wt% on the sample surface, less than half that (3.2 wt%) on the SiW₂₀-Al surface. The coke content of the SiW₂₀-Al/Zr₁₀ sample was 69.2% less than the coke content (2.2 wt%) reported for a 30HZ-20A catalyst with strong Brönsted acidic sites [33]. After 12 h of catalytic activity testing, the amount of coke on the SiW₂₀-Al/Zr₁₀ catalyst surface was 3.1 wt%. A catalyst tolerates a coke content of about 6–10 wt%, with limited activity loss, particularly when the coke is deposited on inactive sites [57,58]. All these findings strongly support our initial hypothesis that γ -Al₂O₃ NPs can tune the acidity and enhance the amount of Lewis acidic sites, leading to a significant reduction in coke deposition on the sample surface. The second hypothesis, i.e., that ZrO₂ could improve the stability and robustness of the catalyst, was proven by increasing the weak acid strength.

Table 8

Coke contents on used catalyst surfaces at different reaction temperatures.

Catalyst	Temperature (°C)	C (wt%)
SiW ₁₀ -Al	280	3.1
	300	2.8
	320	3.1
SiW ₂₀ -Al	280	2.4
	300	3.2
	320	4.6
SiW ₃₀ -Al	280	5.9
	300	3.9
	320	6.5
SiW ₄₀ -Al	280	4.2
	300	4.7
	320	7.6
SiW ₂₀ -Al/Zr ₁₀	300	1.3 (3.1) ^a
SiW ₂₀ -Al/Zr ₂₀	300	3.5
SiW ₂₀ -Al/Zr ₃₀	300	4.3

^a Coke content after 12 h.

Fig. 7. Glycerol conversions and acrolein selectivities versus time for SiW₂₀-Al/Zr₁₀ (a), SiW₂₀-Al/Zr₂₀ (b), and SiW₂₀-Al/Zr₃₀ (c) samples at 300 °C, 12 h reaction time, 2 mL/h glycerol feed, and 20 mL/min carrier gas flow; (d) long-term stability of SiW₂₀-Al/Zr₁₀ sample for 40 h.

3.9. Diffusion study

3.9.1. Internal diffusion

The presence of internal diffusion in glycerol dehydration to acrolein over the SiW₂₀-Al/Zr₁₀ catalyst was investigated by changing the pellet diameter (d_p) at a constant contact time. The gas mass feed flow rate (m_g) and catalytic bed volume (V_{cat}) were also kept constant. Consequently, if the reaction conversion remains constant, this means that there is no internal diffusion to limit the reaction rate [59].

The prepared catalysts were divided into four d_p sizes (0.5, 2, 5, and 20 μ m) based on the FESEM and electron microscopy results [60]. Internal diffusion experiments were performed under the conditions V_{cat} = 2 mL and m_g = 2.55 g/h with various d_p values. Fig. 8(a) shows that for d_p = 20 μ m, internal diffusion limited the reaction and glycerol conversion decreased from 97%–95% to 72%.

3.9.2. External diffusion

The presence of external diffusion was evaluated by varying

m_g and V_{cat} while keeping d_p constant. Changing m_g in a packed-bed reactor with a constant cross-sectional area changes the retention time. Therefore, to keep the retention time constant, V_{cat} must be varied. Consequently, if the glycerol conversion remains constant under different conditions, this shows that external diffusion did not limit the apparent reaction rate [59].

Experiments to determine the presence of external diffusion in glycerol dehydration to acrolein were performed at a constant catalyst (SiW₂₀-Al/Zr₁₀) particle size, i.e., d_p = 5 μ m, but V_{cat} (2, 5, 8, and 10 mL) and m_g (2.55, 6.3, 10.1, and 12.6 g/h) were varied. Fig. 8(b) shows the conversions under various conditions. The profiles show that in the experimental runs, the glycerol conversion was constant, at 95%–97%, for various m_g and V_{cat} values, indicating no limitation by external diffusion. The negligible reduction (1%–2%) in conversion can be attributed to experimental errors. The maximum volume of the catalytic bed was 10 mL because of reactor size limitation.

3.10. RSM modeling of glycerol dehydration to acrolein

Fig. 8. (a) Experimental evaluation of internal diffusion at various pellet sizes (d_p), (b) experimental evaluation of external diffusion at various mass feed flow rates (m_g) and catalytic bed volumes (V_{cat}).

The data-fitting results show that glycerol dehydration to acrolein can be described by a quadratic polynomial model. The best acrolein selectivity prediction model, based on coded factors, is expressed by Eq. (6):

$$\text{Acrolein selectivity (\%)} = +87.34 + 1.58A + 4.15B + 0.23C -$$

Table 10

Central composite design of three independent variables with experimental and RSM-predicted response values.

Run	Tem. (°C)	Cat. amount (g)	Glycerol con. (wt%)	Experimental AC sel. (%)	RSM prediction AC sel. (%)
1	285	0.30	5.38	60.00	60.03
2	315	0.30	5.38	68.00	67.83
3	285	0.70	5.38	63.25	62.84
4	315	0.70	5.38	76.83	76.60
5	285	0.30	15.13	65.60	65.59
6	315	0.30	15.13	58.00	58.16
7	285	0.70	15.13	73.50	73.42
8	315	0.70	15.13	72.24	71.96
9	270	0.50	10.25	58.50	58.91
10	330	0.50	10.25	65.10	65.24
11	300	0.10	10.25	60.70	60.57
12	300	0.90	10.25	76.80	77.18
13	300	0.50	0.50	49.20	49.47
14	300	0.50	20.00	50.40	50.38
15	300	0.50	10.25	87.20	87.34
16	300	0.50	10.25	87.00	87.34
17	300	0.50	10.25	87.40	87.34
18	300	0.50	10.25	87.50	87.34
19	300	0.50	10.25	81.10	87.34
20	300	0.50	10.25	87.60	87.34

$R^2 = 0.999$
Pred $R^2 = 0.998$
Adj $R^2 = 0.999$

$$6.32A^2 - 4.62B^2 - 9.35C^2 + 1.49AB - 3.81AC + 1.26BC \quad (6)$$

where A is the reaction temperature, B is the catalyst loading, and C is the glycerol feed concentration. The model F -value of 437.82 confirms that it is significant. The Prob > F -value is less than 0.05, showing that the model terms are significant. As a result, all the model terms (A , B , C , A^2 , B^2 , C^2 , AB , AC , and BC) are significant (Table 9). The number of experiments, conditions, and experimental and RSM predicted results are summarized in Table 10. The high R^2 (0.999) indicates that the quadratic model adequately represents the actual relationship between the reaction parameters and the response.

3.10.1. Effects of reaction parameter interactions on acrolein selectivity

Table 9

Results of analysis of variance tests.

Source	Sum of square	Degree of freedom	Mean square	F-value	Prob > F	
Model	3246.24	9	360.69	3941.16	<0.0001	Significant
A	40.07	1	40.07	437.76	<0.0001	
B	275.73	1	275.73	3012.76	<0.0001	
C	0.84	1	0.84	9.15	0.0128	
A^2	1003.26	1	1003.26	10962.20	<0.0001	
B^2	535.92	1	535.92	5855.80	<0.0001	
C^2	2200.08	1	2200.08	24039.48	<0.0001	
AB	17.76	1	17.76	194.07	<0.0001	
AC	115.82	1	115.82	1265.57	<0.0001	
BC	12.65	1	12.65	138.23	<0.0001	
Residual	0.92	10	0.092			
Lack of fit	0.64	5	0.13	2.27	0.1948	Not significant
Pure Error	0.28	5	0.056			
Core total	3247.15	19

Fig. 9. Effects of reaction parameter interactions on acrolein selectivity. (a) interaction between glycerol feed concentration and catalyst loading; (b) interaction between reaction temperature and glycerol feed concentration.

The three-dimensional plot in Fig. 9(a) shows the acrolein selectivity as a function of catalyst loading and glycerol feed concentration at 300 °C. Increasing the glycerol concentration from 0.5 wt% to 10.2 wt% and the catalyst loading from 0.1 wt% to 0.5 wt% significantly increases the acrolein selectivity to 87.3%. However, increasing the catalyst loading and glycerol concentration above 0.5 wt% and 10.2 wt%, respectively, decreases the acrolein selectivity. The changes in the catalytic performance are attributed to a decrease in the number of active sites and carbon deposition on the catalyst surface [61]. However, Yadav et al. [9] reported that increasing the amount of catalyst did not seriously affect the acrolein selectivity and only increased the reaction conversion.

Fig. 9(b) shows the effects of interactions between the reaction temperature and glycerol feed concentration on acrolein selectivity at a catalyst loading of 0.5 wt%. The perfect bowl shape in Fig. 9(b) confirms that the reaction temperature and glycerol concentration significantly affect the acrolein selectivity. It is evident that increasing the reaction temperature and glycerol concentration up to the optimal values of 300 °C and 10.2 wt% significantly increase the acrolein selectivity from about 26.2% to 87.3%. However, beyond the optimal values, the acrolein selectivity decreases significantly. Higher glycerol concentrations decrease the catalytic activity because glycerol condenses on the catalyst surface, particularly at low temperatures [32]. A higher reaction temperature enhances coke deposition on the catalyst surface and greatly decreases the catalytic activity [26].

3.10.2. Optimization of process conditions

The dehydration of glycerol was optimized using RSM to obtain the highest acrolein selectivity. The predicted selectivity was 87.7% under the optimal conditions of 10 wt% glycerol feed concentration, 300 °C reaction temperature, and 0.5 wt% catalyst loading. The results are in agreement with the experimental acrolein selectivity of 87.3%, with an error of only 0.4%.

4. Conclusions

A series of supported silicotungstic acid catalysts were synthesized and their catalytic activities were investigated under various conditions, namely temperature 270–330 °C, glycerol feed concentration 0.5–20 wt%, and catalyst loading 0.1–0.9 wt%. The activity results show that SiW₂₀-Al/Zr₁₀ has long-term stability and high selectivity for acrolein. The use of γ-Al₂O₃ NPs and ZrO₂ significantly tunes the acidity and gives large-diameter (>19 nm) pores; this increases the activity and stability of the catalyst. RSM optimization showed that 87.7% acrolein selectivity at 97.0% glycerol conversion could be obtained at 300 °C, 0.5 wt% catalyst, and 10 wt% feed concentration over the SiW₂₀-Al/Zr₁₀ catalyst. Mass transfer limitation studies confirmed the absence of internal and external diffusion at pellet sizes less than 20 μm. These results provide useful data for future simulation studies and catalyst commercialization.

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Graphical Abstract

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Coke-tolerant $\text{SiW}_{20}\text{-Al/Zr}_{10}$ catalyst for glycerol dehydration to acrolein

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A coke-tolerant catalyst ($\text{SiW}_{20}\text{-Al/Zr}_{10}$), which gave 87.3% selectivity for acrolein and 97% glycerol conversion under the conditions 300 °C, 0.5 wt% catalyst, and 10 wt% feed concentration, was synthesized.

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容碳的SiW₂₀-Al/Zr₁₀催化剂用于甘油脱水制丙烯醛

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摘要: 将一系列负载型硅钨酸催化剂用于甘油脱水制丙烯醛反应中。表征结果表明, 最终所得催化剂具有高的热稳定性、大的孔径、强的L酸位和大的比表面积。X射线光电子能谱中清晰地出现归属于W (W 4f = 35.8 eV), Al (Al 2p = 74.9 eV)和Zr (Zr 3d = 182.8 eV)元素的谱峰。在SiW₂₀-Al/Zr₁₀催化剂上丙烯醛选择性最高, 为87.3%, 此时甘油转化率为97%。由于高浓度L酸位的存在, 显著降低了催化剂表面积碳量, 因而该催化剂即使反应40 h之后仍具有较高地催化生成丙烯醛的活性和选择性。响应面方法表明, 在以下优化条件下反应甘油转化率和丙烯醛选择性分别达87.7%和97.0%: 催化剂用量0.5 wt%, 进料甘油浓度10 wt%, 反应温度300 °C。传质限制评估结果显示, 当颗粒尺寸 $d_p < 20\ \mu\text{m}$ 时, 反应不存在内外扩散限制。综上可见, 强L酸催化剂有望用于甘油脱水制丙烯醛反应中。

关键词: 甘油; 脱水; 丙烯醛; 多相催化; 杂多酸

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