



## Research article

Acetalization of glycerol and benzaldehyde to synthesize biofuel additives using  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalystRajeshwari M. Kulkarni<sup>\*</sup>, N. Arvind

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## ABSTRACT

Synthesis of 1,3-dioxane and 1,3-dioxolane, using sulfated  $\text{CeO}_2\text{-ZrO}_2$  catalyst for acetalization of glycerol with benzaldehyde, is the focus of present work.  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst was synthesized using combustion method. Experiments were carried out to analyze the effect of various solvents (n-hexane, toluene, tert-butyl alcohol, pentanol), molar ratios (1:3, 1:5, 1:7), catalyst loadings (3 wt%, 5 wt%, 9 wt %) and temperatures (80 °C, 90 °C, 100 °C) on glycerol conversion and selectivity of the products. Selectivity of 87.20% dioxolane and 12.80% dioxane was obtained at molar ratio of 1:3, 9 wt% catalyst loading and temperature of 100 °C. Strong  $\text{NH}_3$  desorption peak from  $\text{NH}_3\text{-TPD}$  study indicated the high acidic strength of sulphated catalyst. Strong surface acidity and surface porosity (observed from TEM and SEM analysis) contributed to an enhanced activity of the catalyst for glycerol acetalization reaction. The kinetics of the reaction was studied using an elementary kinetic law. A correlation coefficient of 0.98 from the selected kinetic model proved that the rate of acetalization reaction was dependent on glycerol concentration and acetal formation was instantaneous. The study demonstrated the application of an environmentally benign, inexpensive, thermally stable, active  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst for glycerol acetalization reaction to synthesize 1,3-dioxolane as the desired product.

## 1. Introduction

The biodiesel industry has gained prominence over traditional fossil fuel-based diesel industry, hence much of the current research involves searching for ways to utilize the by-products; biomass and crude glycerol. Properties of biodiesel such as lubricity, high flash point, close heat combustion, viscosity, limited exhaust emissions and superior cetane number make it more attractive (Al-Mashhadani and Fernando, 2013; Kulkarni et al., 2020). With the rapidly expanding biodiesel industry, a glut of crude glycerol (approximately 10%) is also being generated, resulting in the drastic reduction of fuel yield (Alhanash et al., 2007; Adhikari et al., 2009; Calvino-Casilda et al., 2014). Therefore, methods to utilize this glycerol to synthesize products of high value must be innovated (Johnson and Taconi, 2007). Among the various chemical and biological routes for glycerol value addition, acetalization and etherification reactions have been tested by various researchers. These reactions produce oxygenate blending stock for diesel to improve the total yield and quality of diesel by reducing emissions through decreasing viscosity and cloud points (Carraretto, 2004; Ayoub and Abdullah, 2012).

In recent years' significant research efforts have been spent on glycerol acetalization reaction with various carbonyl compounds such as aldehydes, ketones, furfural, levulinic acid etc. The products obtained from the reactions are cyclic isomeric acetals, namely 1,3-dioxolane (five-membered ring) and 1,3-dioxane (six-membered ring) (Fan et al., 2012; Agirre et al., 2013; Pradima et al., 2017). Acetalization of glycerol is a significant reaction as it gives rise to environmentally friendly and economically feasible products, which can act as biodiesel and food additives. 1,3-dioxolane and 1,3-dioxane, biofuel additives are presently prepared by reacting carbonyl compounds with aldehydes in the presence of Brønsted or Lewis acid catalysts. 1,3-dioxane and 1,3-dioxolane are used as low-temperature heat transfer fluids, solvents, adhesives and stabilizers in construction industries. Acetals are also used widely in fuel, food, cosmetic, beverage and pharmaceutical industries (Deutsch et al., 2007).

1,3-dioxane or m-dioxane is a chemical compound with the molecular formula  $\text{C}_4\text{H}_8\text{O}_2$ . It is a clear colorless liquid and is soluble in water, ethanol, acetone and benzene. Dioxane is used as a stabilizer and as a solvent for a range of practical applications. 1,3-dioxane is also employed as an additive for diesel fuels, as bases for surfactants and as scents or

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flavors in food (Zaher et al., 2017; Nda-Umar et al., 2019). 1,3-dioxolane is a heterocyclic acetal with the chemical formula  $(\text{CH}_2)_2\text{OCH}_2$  and is related to tetrahydrofuran by interchange of an oxygen atom for a  $\text{CH}_2$  group. 1,3-dioxolane is used as a solvent and as a co-monomer in poly-acetals. It is a clear colorless liquid, slightly denser than water and its vapors are heavier than air. 1,3-dioxolane possesses excellent solvent and fuel additive properties, non-carcinogenic, non-teratogenic and causes no ozone-related problems. 1,3-dioxolane and 1,3-dioxane find extensive applications in construction, food, pharmaceutical, cosmetics, beverage and majorly in fuel industries. These acetals are considered as excellent ignition accelerators, fuel additives and antiknock additives (Trifoi et al., 2016; Devi and Dalai, 2020).

Several studies on the synthesis of these cyclic isomeric products have reported that by varying the influential reaction parameters and a suitable catalyst, the product yield and selectivity towards acetals could be increased. Researchers have reported the application of homogeneous catalyst (toluenesulfonic acid,  $\text{H}_3\text{PO}_4$ , HCl or acidic ionic liquids) and heterogeneous catalyst (Montmorillonite, zeolite, amberlyst,  $\text{MoO}_3/\text{SiO}_2$ ,  $\text{TiO}_2\text{-ZrO}_2$ ) for glycerol acetalization reaction (Climent et al., 2004; Pradima et al., 2017). Table 1 summarizes various catalysts used for synthesis of isomeric acetals viz. 1,3-dioxolane and 1,3-dioxane.

In this study, acetalization was used to valorise glycerol using benzaldehyde as carbonyl compound as shown in Figure 1. Sulfated cerium and zirconium metal oxide catalyst produced by the combustion method was used as a heterogeneous catalyst. Due to enhanced surface acidic properties and superior physicochemical properties, the mixed metal oxide catalyst was preferred over individual oxides. Advantages of  $\text{CeO}_2$  such as resistance to heat, oxygen storage capacity and redox enhanced property and benefits of  $\text{ZrO}_2$  such as high concentration of hydroxyl ions and coordinating unsaturated cationic Lewis acid sites are blended in the combustion method of synthesis of  $\text{CeO}_2\text{-ZrO}_2$  catalyst (Kambolis et al., 2010; Bagheri et al., 2015). Time and energy-efficient, solution combustion synthesis involved self-sustaining reaction of metal salts as oxidants and fuel as reductant. Based on the literature, there is no research work reported on utilization of sulfated  $\text{CeO}_2\text{-ZrO}_2$  for glycerol acetalization reaction. The present work focuses on increasing glycerol conversion and selectivity towards five-membered ring acetal 1,3-dioxolane, which is an excellent fuel additive. Effect of factors influencing the selected reaction such as solvent, mole ratio, catalyst dosage and temperature were analyzed and a suitable kinetic model was proposed.

## 2. Materials and methods

### 2.1. Chemicals

AR Grade cerium (III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) and zirconium nitrate ( $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ) supplied by Himedia Laboratories Pvt. Ltd were used to prepare mixed oxide catalyst using urea ( $\text{CO}(\text{NH}_2)_2$ ) (SD Fine Chemicals Ltd) as the reductant. Sulfonation of catalyst was carried out using sulphuric acid (Nice Chemical Pvt. Ltd).

Benzaldehyde, glycerol and the solvents (toluene, tert-Butanol, pentanol and n-hexane) required for acetalization reaction were procured from Fischer Scientific Ltd.

### 2.2. Catalyst preparation

$\text{CeO}_2\text{-ZrO}_2$  mixed oxide catalyst was synthesized by combustion method. Solution combustion synthesis involves a self-sustained reaction between mixture of cerium and zirconium nitrates and urea as fuel. 4.3423g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 4.2933g of  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  were used as oxidizers and 3.5 g of urea was used as a reducing fuel in the combustion method. Metal nitrates and urea were mixed thoroughly with distilled water in a crucible and combusted at a high temperature in a muffle

furnace. The  $\text{CeO}_2\text{-ZrO}_2$  catalyst synthesized was then sulphated to enhance the activity of the acid sites. After combustion, 5 mL of  $\text{H}_2\text{SO}_4$  per gram of  $\text{CeO}_2\text{-ZrO}_2$  was added to the reaction mixture to prepare sulphated metal oxide catalyst. This mixture was then stirred using a magnetic stirrer, dried in the hot air oven and finally calcined in the muffle furnace at 500 °C for 3 h to obtain  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst.

### 2.3. Experimental setup

Acetalization reaction between glycerol and benzaldehyde was catalyzed by  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  in a two-necked round bottom flask. Continuous stirring was done using IKA RET control-visc Magnetic stirrer (Ultra instruments) and reaction temperature was maintained constant. 20 mL of solvent was added to 50 mL of reaction mixture and the reaction was carried out for 8 h. A condenser was fitted over the central neck of the flask to avoid any evaporation of the contents. The temperature of the reaction mixture was monitored at regular time intervals. The round bottom flask was placed on a Petri dish containing oil, which ensures uniform circulation of heat to the contents of the flask. Stirring speed was maintained at a constant 500 rpm for all the experimental runs conducted. At various intervals of time, samples of definite volume were withdrawn, centrifuged and the supernatant was analyzed using a Gas Chromatograph.

### 2.4. Analysis

Reaction samples were analyzed by Gas Chromatograph with FID (1100 from Mayura analytical LLP), equipped with a Silphenylene polysiloxane capillary column. The centrifuged samples were taken in vials and injected into the column. Nitrogen ( $\text{N}_2$ ) acts as the Carrier Gas with a flow rate of 35 mL/min. The column temperature was set to 473 K and oven was set to 523 K and the column was eluted for 30 min. After elution, the column temperature was set to 393 K and the sample was injected. The concentration of reactants (glycerol and benzaldehyde) and products (1,3-dioxolane and 1,3-dioxane) were detected in the sample based on their retention time.

## 3. Results and discussion

### 3.1. Characterization of $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ catalyst

Figures 2, 3 and 4 depict the surface images of sulfated mixed oxide obtained by the Transmission Electron Microscope (TEM) and Scanning electron microscope (SEM).  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  sample appear as collection of randomly oriented tiny particles of approximately 170 nm particle size. The EDS Spectra of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  as shown in Figure 5, indicates the intensity of each configuration of the element of the prepared catalyst at various instances of energy. The composition of the sample in terms of an atomic and mass fraction is presented in Table 2. The EDS spectrum confirms the presence of cerium and zirconium in the sample.

Barrett Joyner Halenda – BJH analysis (Figure 6) of mesoporous  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst from nitrogen adsorption data indicated that pore size was 3.32 nm (type IV isotherm) and pore volume 0.0318  $\text{cm}^3/\text{g}$ . Surface area was found to be 21.63  $\text{m}^2/\text{g}$ .

The measurement of acidity of the metal oxide catalysts (temperature-programmed desorption of ammonia  $\text{NH}_3\text{-TPD}$ ) was accomplished by Bel-Cat (Bel Japan Inc.) instrument. The metal oxide was preheated at 300 °C under helium flow for 3 h and then cooled to 80 °C. The surface of the metal oxide catalyst was saturated with  $\text{NH}_3$  gas for 30 min. The  $\text{NH}_3$  gas adsorbed in excess was purged with helium flow for an hour. The TPD of  $\text{NH}_3$  was measured by heating from the ambient temperature at 10 °C/min until 700 °C. The sulfated catalyst showed desorbed peaks mainly over the region of 300–700 °C, which according to literature, can be

**Table 1.** Different catalyst reported in the literature for acetalization reaction of glycerol with various carbonyl compounds.

Carbonyl compound	Catalyst	Reaction conditions	Conversion, %	Selectivity %		Reference
				Five-membered, %	Six-membered, %	
Phenylacetaldehyde	zeolite USY-2 (Si/Al = 35)	molar ratio glycerol to aldehyde = 2:1 catalyst loading = 7.5 wt% solvent = 40 mL toluene reaction time = 1h reaction temperature = 420K	93	58	35	<a href="#">Climent et al., 2004</a>
Benzaldehyde	Amberlyst-36	molar ratio glycerol to aldehyde = 1.1:1, catalyst loading = 0.5 g solvent = 0.1 g toluene reaction time = 2h reaction temperature = 357–383K	–	39	61	<a href="#">Deutsch et al., 2007</a>
Formaldehyde			–	35	65	
Benzaldehyde	Toluene sulfonic acid SiO <sub>2</sub> 1% MoO <sub>3</sub> /SiO <sub>2</sub> 10% MoO <sub>3</sub> /SiO <sub>2</sub> 20% MoO <sub>3</sub> /SiO <sub>2</sub>	molar ratio of glycerol to aldehyde = 1.1:1 catalyst loading = 10wt% solvent = 15g toluene reaction time = 8h reaction temperature = 373 K	81	37	63	<a href="#">Umbarkar et al., 2012</a>
			23	50	50	
			37	37	63	
			43	37.5	62.5	
			72	40	60	
p-Tert-butyl benzaldehyde	20% MoO <sub>3</sub> /SiO <sub>2</sub>		54	38	62	
2-Hydroxy,5-nitro benzaldehyde			23	40	60	
Anisaldehyde			45	0.5	99.5	
o-Chloro Benzaldehyde			61	28	72	
n-Heptaldehyde			78	38	62	
n-Butyraldehyde			69	34	66	
Trans-cinnamaldehyde			10	00	100	
Phe nylacetaldehyde			56	09	91	
Butanaldehyde	Amberlyst-15	molar ratio of glycerol to aldehyde = 1:1.05 catalyst loading = 0.36g solvent = 5mL dimethylsulfoxide Reaction time = 24h Reaction temp = 343 K	85	80	20	<a href="#">Silva et al., 2010</a>
Formaldehyde	Amberlyst-47	molar ratio of glycerol to aldehyde = 1:1 catalyst loading = 5wt% Reaction time = 12h Reaction temp = 353 K	50	00	100	<a href="#">Agirre et al., 2011</a>
acetaldehyde	Amberlyst-47	molar ratio of glycerol to aldehyde = 3:1 catalyst loading = 2wt% Reaction time = 10h Reaction temp = 313 K	100	00	100	<a href="#">Agirre et al., 2013</a>
Benzaldehyde	MoO <sub>x</sub> /TiO <sub>2</sub> -ZrO <sub>2</sub>	molar ratio of glycerol to aldehyde = 1:1 catalyst loading = 5wt.% Reaction time = 30 min Reaction temperature = 373 K.	74	49	51	<a href="#">Sudarsanam et al., 2013</a>
o-Chloro benzaldehyde			55	37	63	
p-Chloro benzaldehyde			71	43	57	
p-Anisaldehyde			22	23	77	
m-Nitro benzaldehyde			60	32	68	
p-Nitro benzaldehyde			62	28	72	
paraformaldehyde	Fe/Al-SBA-15	molar ratio of glycerol to aldehyde = 1:2 catalyst loading = 20 mg Reaction time = 8h Reaction temperature = 373 K.	100	24	76	<a href="#">Gonzalez-Arellano et al., 2014</a>
Benzaldehyde		molar ratio of glycerol to aldehyde/acetone = 1:1 catalyst loading = 50 mg Reaction time = 8h Reaction temperature = 373 K.	70	84	16	
Acetone			51	99	1	
Furfural		molar ratio of glycerol to furfural = 1:1.5 catalyst loading = 50 mg Reaction time = 12h Reaction temperature = 373 K	95	60	40	
Acetaldehyde	FeCl <sub>3</sub> ·6H <sub>2</sub> O	molar ratio of glycerol to aldehyde = 1:1	58	41	59	<a href="#">Zaher et al. (2017)</a>
Benzaldehyde			51	39	61	

(continued on next page)

Table 1 (continued)

Carbonyl compound	Catalyst	Reaction conditions	Conversion, %	Selectivity %		Reference
				Five-membered, %	Six-membered, %	
Acetone	FeCl <sub>3</sub> ·6H <sub>2</sub> O	catalyst loading = 54 mg solvent = Tetrahydrofuran 1mL Reaction time = 3h Reaction temperature = 333 K molar ratio of glycerol to acetone = 1:1 catalyst loading = 54 mg solvent = Tetrahydrofuran 1mL Reaction time = 1h Reaction temperature = 333 K	100	98	2	
Furfural	Montmorillonite-K-10 SC Zeolite SBA-15 SC	molar ratio of glycerol to Furfural = 1:1 catalyst loading = 5 wt % Reaction time = 2h Reaction temperature = 313 K	62 74	75 62	11 6	Gutiérrez-Acebo et al., 2018
Acetone	VO <sub>x</sub> NT NiVO <sub>x</sub> NT CoVO <sub>x</sub> NT PtVO <sub>x</sub> NT	molar ratio of glycerol to acetone = 1:1 catalyst loading = 130 mg Reaction time = 6h Reaction temperature = 323 K	69.2 67.1 50.4 54.3	17 22 24 19	1.4 1.9 2.0 1.6	Pinheiro et al., 2019
Benzaldehyde	SO <sub>4</sub> <sup>2-</sup> /CeO <sub>2</sub> -ZrO <sub>2</sub> catalyst	molar ratio of glycerol to aldehyde = 1:3 catalyst loading = 9 wt% Reaction time = 8h Reaction temperature = 373K	91.8	87.2	12.8	Present study

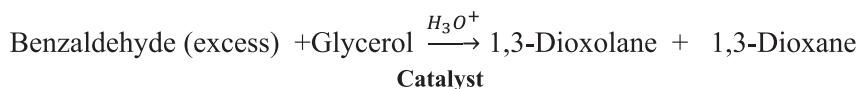


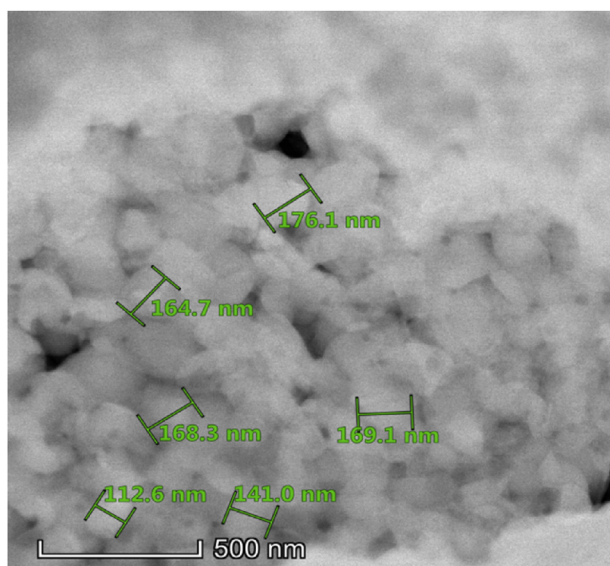
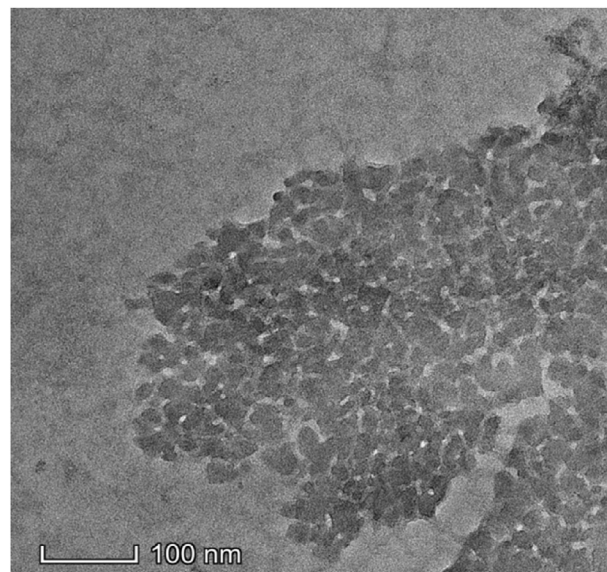
Figure 1. Acetalization reaction between benzaldehyde and glycerol.

considered as a region of medium-strong acid sites (Figure 7). The total amount of desorbed NH<sub>3</sub> on the metal oxide was 236 μmol/g.

The properties of the catalysts were determined based on the temperature profile obtained from TPD analysis in the weak region (<200 °C), moderate region (200–450 °C), and the strong region (>450 °C) (Kumar et al., 2016; Glorius et al., 2018). Sulfated CeO<sub>2</sub>-ZrO<sub>2</sub> metal oxide exhibited three desorption maxima at around 400 °C, 600 °C and 700 °C indicating relevant acidic sites with two different acid strengths. The peak at 400 °C represents acidic sites of medium strength and the

peak at 600 °C and 700 °C correspond to strong Lewis acid sites. Shah et al., 2019 reported that CeZrO<sub>x</sub> mixed metal oxide catalyst prepared with different Ce-Zr ratios showed two desorption peaks in the range of 350–450 °C and 500–600 °C to indicate the presence of weak and strong acidic sites, which is in concurrence with the present results.

Sulfate incorporation in the CeO<sub>2</sub>-ZrO<sub>2</sub> metal oxides validates additional desorption peak at 700 °C indicating the creation of strong acidic active sites on the surface of the catalyst. Sulphate groups contribute for

Figure 2. TEM Images of SO<sub>4</sub><sup>2-</sup>/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst at 500 nm magnification.Figure 3. TEM Images of SO<sub>4</sub><sup>2-</sup>/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst at 100 nm magnification.

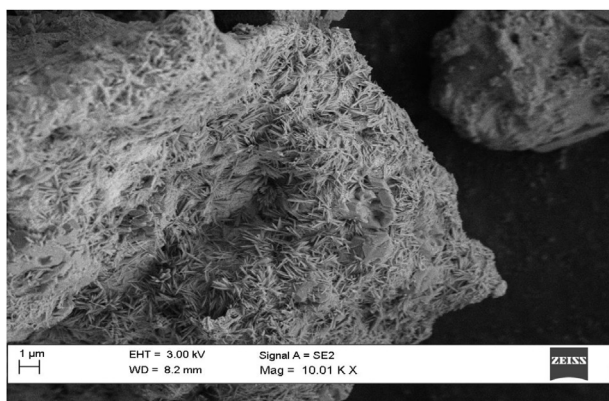


Figure 4. SEM Image of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst.

Lewis acid sites and attract electrons to produce Lewis acid centers on the oxide surfaces. Transition from ionic to covalent due to calcination and bonding with S=O contributed to generation of strong acid sites. Similar observation was reported by Reddy et al. (2006) and Abida and Ali (2020). High acidic strength (236  $\mu\text{mol/g}$ ) and the porous surface have contributed to the superior activity of the prepared catalyst for glycerol acetalization reaction.

Thermogravimetric analysis (TGA) was performed on a thermo-gravimetric instrument (NETZSCH STA 449FS type) and the obtained thermogram is presented in Figure 8. 10 mg of sample was placed on an  $\text{Al}_2\text{O}_3$  crucible and was heated from 30 to 800  $^\circ\text{C}$  (10  $^\circ\text{C}/\text{min}$ ) in  $\text{N}_2$  atmosphere to investigate thermal stability of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  synthesized catalyst.

The total weight loss occurred was 13%. For the prepared catalyst, physisorbed water loss was observed at 200  $^\circ\text{C}$  and dehydration from micropores was observed at 650  $^\circ\text{C}$ .

### 3.2. Study of the acetalization reaction of glycerol with benzaldehyde using $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$

Depending on the extent of the reaction carried out, two different products, namely dioxolane and dioxane, were formed. The reaction

Table 2. Composition in terms of atomic and mass fraction obtained from EDS Spectrum graph.

Z	Element	Atomic Fraction (%)	Mass Fraction (%)
6	C	1.83	0.24
8	O	10.09	1.77
16	S	1.44	0.47
40	Zr	33.92	29.05
58	Ce	52.72	68.47

steps involved in the formation of cyclic acetals were as proposed by Sudarsanam et al. (2013) (i) formation of cationic carbonyl carbon of the benzaldehyde through the strong attachment of oxygen atoms of the carbonyl group with sulfated mixed metal oxide catalyst (ii) formation of intermediate benzyl cation when oxygen atom of glycerol attaches to cationic carbonyl carbon (iii) benzyl cation intern gives acetals.

Different solvents, molar ratios of glycerol to benzaldehyde, catalyst loadings and temperatures exhibited variations in the composition and selectivity of the products.

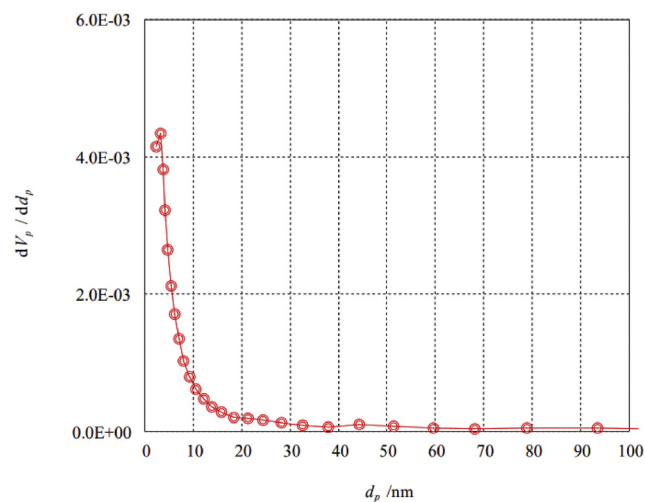


Figure 6. Macropore size distribution of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst.

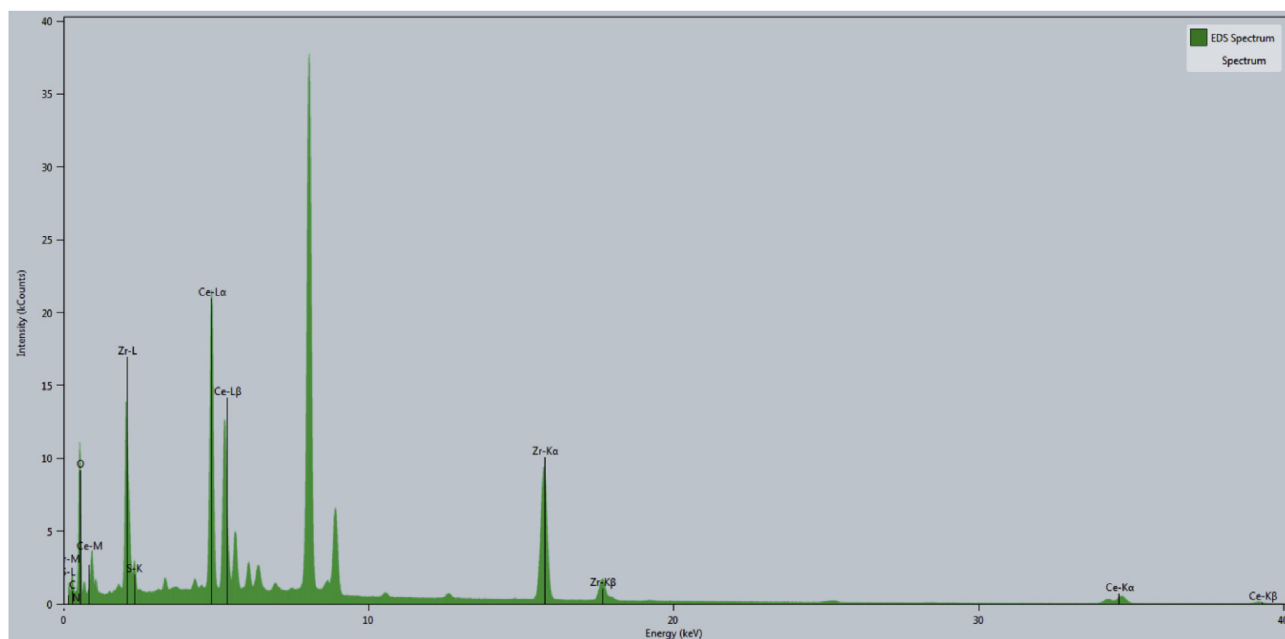


Figure 5. EDS Spectra of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst.

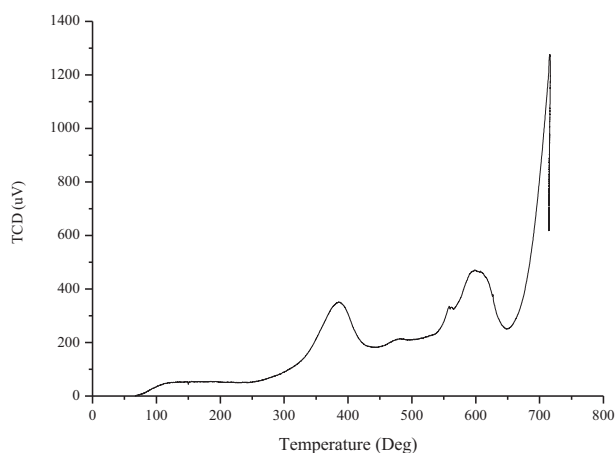


Figure 7. TPD profile of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst.

### 3.2.1. Effect of solvents used for acetalization of glycerol

The effects of different solvents on glycerol acetalization were studied using n-hexane, tert-butanol, pentanol and toluene. Reaction was carried out at 1:3 M ratio of glycerol to benzaldehyde, catalyst loading of 9 wt% at 100 °C for duration of 4 h using 20 mL of solvent at 500 rpm. Higher glycerol conversion of 86% was obtained when toluene was used as a solvent as compared to n-hexane (70%) and tert-butanol (64%). Pentanol did not show any conversion of glycerol to product formation.

Catalytic conversion in hydrophobic solvents such as toluene and hexane was found to be higher than hydrophilic solvents tert-butanol and pentanol. It was observed, solvents with log P i.e. logarithm of partition coefficient value (toluene 2.5 and hexane 3.5) above 2 were more suitable as compared to solvents with a log P value below 2 (tert-butanol 0.80 and Pentanol 1.4). Since log P value is a quantitative measure of solvent polarity, hydrophobic solvents were found to be advantageous. The viscosity of toluene and hexane was lower than the other two solvents. Further, dielectric constant value of toluene 2.38 and hexane 1.88 were lower as compared to tert-butanol 17.8 and pentanol 13.9. It was observed that an inverse correlation exists between dielectric constant and glycerol conversion. A similar observation was also reported by Laane et al., 1987 and Carrea et al., 1995. Steric hindrance and lower solubility of glycerol in hexane compared to toluene was also observed

(Su and Wei, 2008). Hence, it was concluded that toluene was the optimum solvent for further studies. The enhanced catalytic performance of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  in toluene might be due to its high boiling temperature that could actively enhance the acetalization of glycerol (Climent et al., 2004; Sudarsanam et al., 2013). Solvent toluene (viscosity 0.56 centi poise) addition into the reaction mixture resulted in reduced viscosity and facilitated strong binding interaction between glycerol and benzaldehyde (Agirre et al., 2013).

### 3.2.2. Effect of molar ratios of glycerol to benzaldehyde

Effect of different molar ratios of glycerol to benzaldehyde, viz. 1:3, 1:5, and 1:7 on glycerol conversion were observed at a reaction temperature of 100 °C, catalyst loading of 9 wt % and reaction time of 8 h (Figure 9). Glycerol conversion of 91.82%, 92.08% and 75.59% were obtained when 1:3, 1:5 and 1:7 M ratios were used respectively. It can be observed that 1:5 M ratio of glycerol to benzaldehyde facilitates relatively higher conversion of glycerol to products compared to 1:3. But the selectivity for dioxalane is better with molar ratio of 1:3 (87.20% dioxalane and 12.80% dioxane) compared to 1:5 (82.33% dioxalane and 17.67% dioxane). Molar ratio 1:3 is economically favourable as more product concentration was obtained with a lesser quantity of benzaldehyde and with a minimal decrease in conversion. Excessive amount of benzaldehyde hinders the reaction by dominating over a low quantity of glycerol, which is an undesirable outcome. The access for reactant molecules to reach acid sites of catalyst decreases with increase in molar ratio (Serafim et al., 2011; Güemez et al., 2013).

### 3.2.3. Effect of catalyst loading

The effect of catalyst loading on the acetalization of glycerol with benzaldehyde was analyzed with 3 wt%, 5 wt% and 9 wt% catalyst loading for a molar ratio of 1:3 of glycerol to benzaldehyde at a reaction temperature of 100 °C for a reaction mixture volume of 50 mL for 8 h using 20 mL toluene as solvent at 500 rpm.

Glycerol conversion was found to increase from 61.47% to 73.89% at 3 wt%; 72.56%–84.42% at 5 wt%; 82.34%–91.82% at 9 wt% with the increase in reaction time from 30 min to 480 min (Figure 10). The kinetics depend on the catalyst porosity; the catalyst matrix must allow the reactants to diffuse through it, to reach the active sites. The rapid phase of glycerol conversion was observed during 30 min–120 min of reaction time, as more binding sites and high concentration gradient were available for reaction to occur. Increase in percentage saturation, reduction in

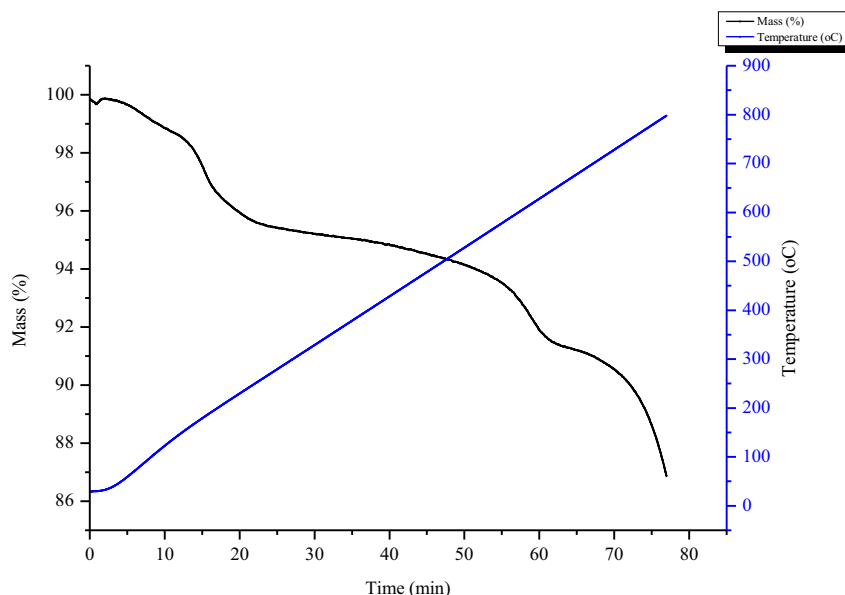


Figure 8. TGA profile of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst.

active sites and mass transfer limitations resulted in slow phase from 120 min to 480 min. The conversion was almost constant after the reaction time of 8 h.

An increase in the catalyst loading from 3 wt% to 9 wt%, increased the conversion of glycerol in the acetalization reaction from 73.89% to 91.82%. Calcination at higher temperature increased the number of active sites. An increase in catalyst loading enhanced the number of acidic active sites on the surface of the catalyst available and facilitated more interaction and collision between reactant molecules for the acetalization reaction (Da Silva et al., 2009; Pinheiro et al., 2019). Glycerol conversion was found to be higher with an increase in catalyst loading due to availability of more number of reactive groups and active acidic sites. The conversion reached a maximum and remained constant with further increase in dosage (Sudarsanam et al., 2013). Once the equilibrium was established, there was no further change observed. According to the results obtained, it was inferred that glycerol conversion increased with catalyst concentration, reached a maximum and remained constant with further increase in catalyst weight.

Selectivity of 76.13% dioxolane and 23.87% dioxane at 3wt% catalyst loading, selectivity of 80.34% dioxolane and 19.66% dioxane at 5 wt% catalyst loading and selectivity of 87.20% dioxolane and 12.80% dioxane at 9 wt% catalyst loading were achieved at the reaction condition of 100 °C temperature and 8h reaction time.

The acetalization of glycerol with benzaldehyde involves (i) kinetically controlled stage where formation of dioxolane happened at higher rate compared to dioxane (ii) thermodynamically controlled stage where

dioxolane isomerized to form dioxane (Deutsch et al., 2007; Umbarkar et al., 2012). High selectivity to 1,3- dioxolane a kinetically favoured product when compared to 1,3-dioxane was noted and maximum selectivity was achieved for 1,3 dioxolane in all the cases. Similar observations of higher selectivity to dioxolane were reported by Climent et al. (2004), Silva et al. (2010), Gonzalez-Arellano et al. (2014), Gutiérrez-Acebo et al. (2018).

### 3.2.4. Effect of Temperature

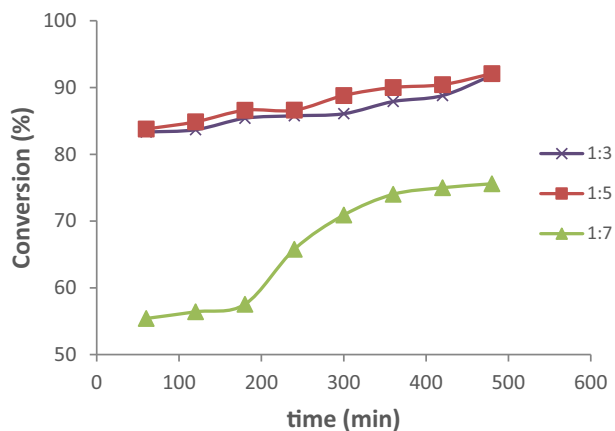
Temperature plays a significant role in catalytic reactions; the reaction temperature is a crucial factor for the acetalization of glycerol (Sudarsanam et al., 2013). With the increase in temperature, the mixture viscosity reduces, mutual solubility increases and the catalytic and reactant interactions are enhanced (Yadav and Devendran, 2012; Kulkarni et al., 2020). Hence, the desired temperature has to be determined to obtain the optimum catalytic activity. Experiments were carried out with the reaction conditions as 9 wt% catalyst loading, 20 mL toluene as solvent, 1:3 M ratio of glycerol to benzaldehyde and 500 rpm at three different temperatures viz 80 °C, 90 °C and 100 °C.

Glycerol conversion of 84.61%, 87.10% and 91.82% was obtained after 8 h contact time when reaction temperatures were maintained at 80 °C, 90 °C and 100 °C respectively. It was found that with the increase in temperature, glycerol conversion increased and the temperature of 100 °C was the most suitable out of the three for optimum catalytic activity (Figure 11). The rise in the temperature facilitated the reactant interactions onto catalyst surface, increasing the active sites and expansion of pores. Selectivity towards 1,3- dioxolane was observed to be dominating over 1,3-dioxane at all temperatures (Selectivity at 80 °C 89.69% dioxolane and 10.31% dioxane; Selectivity at 90 °C 87.54% dioxolane and 12.46% dioxane; Selectivity at 100 °C 87.20% dioxolane and 12.80% dioxane). The reaction between glycerol and benzaldehyde supported with  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst was instantaneous leading to the formation of kinetically favoured product 1,3 dioxolane. The formation of thermodynamically driven isomer 1,3-dioxane was less in all the cases indicating marginal influence of temperature on the acetalization reaction.

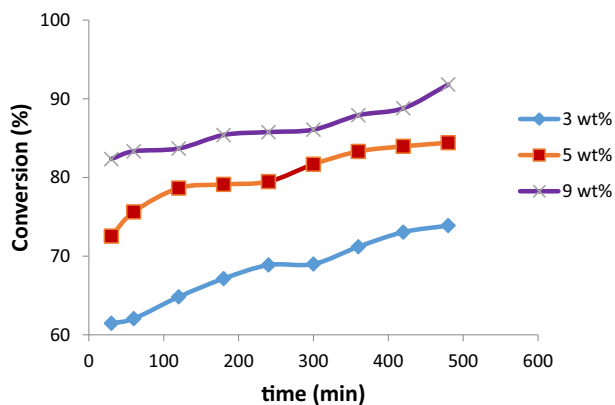
The conversion and selectivity reported in this work are excellent compared to the results reported by different researchers in past with different catalysts (Table 1). It was evident from Table 1 that  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst has higher selectivity for 1,3 dioxolane than many of the other reported catalysts.

### 3.3. Kinetic modelling

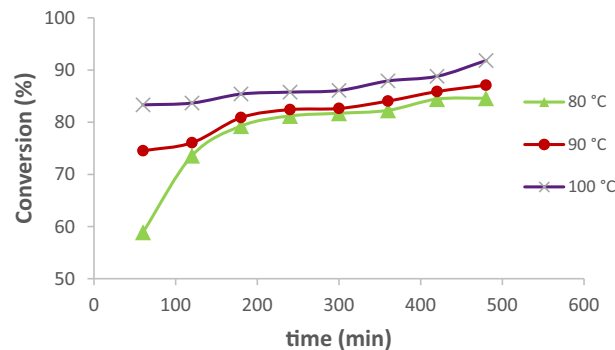
The concentration-time data obtained from the experiment at the condition of 1:3 M ratio, 9 wt% catalyst loading and a temperature of 100 °C in a batch reactor was used for kinetic modeling. The conditions leading to maximum conversion were chosen based on experimental



**Figure 9.** Effect of Molar ratio of glycerol to benzaldehyde on the conversion of glycerol at 100 °C, 9 wt%  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst loading, and 20 mL of Toluene for the reaction time of 8 h at 500 rpm.



**Figure 10.** Effect of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst loading on the glycerol conversion at 100 °C, 1:3 M ratio and 20 mL of solvent for the reaction time of 8 h at 500 rpm.



**Figure 11.** Effect of Temperature on the glycerol conversion at 100 °C, 1:3 M ratio, 9 wt%  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst loading, and 20 mL of solvent for the reaction time of 8 h at 500 rpm.

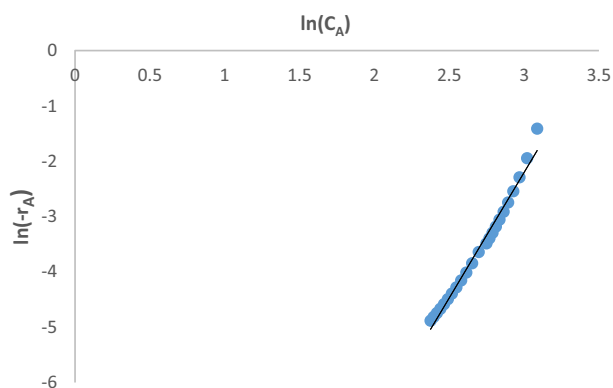


Figure 12. Kinetics of the reaction at 100 °C.

results obtained from effect of catalyst loading. Kinetic analysis helped in providing kinetic information for carrying out industrial-scale glycerol acetalization reaction to produce 1,3-dioxolane and 1,3-dioxane. Since glycerol is the limiting reactant, kinetics was explored by relating the rate of reaction with glycerol concentration using pseudo homogeneous model. In the selected simple model, it was assumed that rate solely depended on glycerol concentration and its attachment to the active sites of catalyst. It was assumed that attachment of the reactants on to catalyst surface and acetalization reaction leading to acetal formation were instantaneous (Agirre et al., 2013; Zhou et al., 2012). Backward reaction was slow and benzaldehyde was supplied in excess, indicating concentration of benzaldehyde in active sites as constant. Rate data obtained at 9 wt% catalyst loading was used in the model (Equation 1). The logarithmic values of the concentration of glycerol and rate were taken and fit into the pseudo homogeneous model (Figure 12) as follows:

$$-r_G = k.C_G^\alpha \quad (1)$$

The data was found to fit the equation well with a regression coefficient ( $R^2$ ) of 0.9831. The values of  $\alpha$  and rate constant ( $k$ ) were determined as 4.5 and  $1.3 \times 10^{-7} (\text{L/g}_{\text{cat}})^{-3} (\text{min})^{-1}$  respectively, from the slope and intercept of the plot.

#### 4. Conclusion

The acetalization of glycerol with benzaldehyde using synthesized mixed metal oxide catalyst  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  was carried out. The catalyst was synthesized by the combustion process. Characterization of the catalyst was done by  $\text{NH}_3$ -TPD, SEM, TEM coupled with EDS analysis. The influence of different parameters such as various solvents, glycerol to benzaldehyde molar ratio, catalyst loading and temperature were studied and the process conditions were optimized.

The research work effectively utilized the stable active combustion-synthesized metal oxide catalysts  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  for spontaneous kinetically controlled glycerol acetalization reaction to produce valuable products that find applications in a wide range of industries. Glycerol conversion of 91.82% was achieved with 87.20% selectivity towards 1,3-dioxolane at reaction conditions of 9 wt% catalyst loading, 20 mL toluene solvent, 1:3 M ratio of glycerol to benzaldehyde and 100 °C temperature.

#### Declarations

##### Author contribution statement

Rajeswari M. Kulakarni: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Arvind N.: Performed the experiments; Wrote the paper.

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#### Data availability statement

Data will be made available on request.

#### Declaration of interests statement

The authors declare no conflict of interest.

#### Additional information

No additional information is available for this paper.

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