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Synthesis of bio-additives: Acetylation of glycerol over zirconia-based solid acid catalysts

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1. Introduction

The indiscriminate extraction and consumption of fossil fuels have led to a reduction in petroleum reserves. The reduction of petroleum reserves, energy security and increase in the emission of greenhouse gases are forcing the scientific community to search for clean and renewable energy sources. Biomass is a renewable and clean energy source, and its derived fuels are attractive alternatives to the fossil fuels and for a variety of chemical intermediates. Glycerol is one of the biomass-derived molecules [1] and it can be obtained as the main byproduct (about 10% w/w) in triglyceride transesterification process during biodiesel production [2–5]. The effective utilization of glycerol into useful chemicals is desirable to reduce both environmental pollution and economical losses [6]. Recently, many studies have been focused on the catalytic conversion of bioglycerol to high value chemicals such as 1,2-propanediol, 1,3-propanediol, acrolein, hydroxyacetone, glyceric acid, esters of glycerol and so on [7]. Acetylation of glycerol is an excellent reaction for the production of acetins (mono-, di- and tri-esters of glycerol) which have good commercial significance. These acetins are primarily used as transportation fuel additives [8,9]. In particular, triacetin is more desirable than other two acetins for mixing with hydrocarbon fuels. The addition of small amounts of triacetin improves the cold and viscosity properties of biodiesel. Triacetin could be used as an antiknock additive for gasoline [9]. Also acetins are of great value in food, cosmetic and pharmaceutical industries. Acetins are

ABSTRACT

Acetylation of glycerol with acetic acid was investigated over ZrO2, TiO2-ZrO2, WOx/TiO2-ZrO2 and MOOx/ TiO₂-ZrO₂ solid acid catalysts to synthesize monoacetin, diacetin and triacetin having interesting applications as bio-additives for petroleum fuels. The prepared catalysts were characterized by means of XRD, BET surface area, ammonia-TPD and FT-Raman techniques. The effect of various parameters such as reaction temperature, molar ratio of acetic acid to glycerol, catalyst wt.% and time-on-stream were studied to optimize the reaction conditions. Among various catalysts investigated, the MoO_x/TiO₂-ZrO₂ combination exhibited highest conversion (~100%) with best product selectivity, and a high time-on-stream stability. © 2010 Elsevier B.V. All rights reserved.

> also employed for various purposes, for example, in the manufacture of explosives and plasticizers, as solvents for printing ink, dyestuffs and antiseptics, as softening and emulsifying agents and so on [10,11]. Acetylation is an acid catalyzed reaction and conventionally carried out using mineral acids as catalysts. In view of the environmental and economical reasons, there is a tremendous effort to replace the conventional liquid acid catalysts with solid acids. There are some attempts on the acetylation of glycerol by using different solid acid catalysts such as amberlyst, niobic acid, heteropolyacids, zeolites and other [11–14]. Most of the reported catalysts showed poor conversion of glycerol and less selectivity towards the desired product. On the other hand solid acid catalysts such as ion exchange resign (amberlyst) and heteropolyacids exhibit poor thermal stability, poor regeneration ability and low specific surface area [15,16]. Supported heteropolyacids having high surface area and better thermal stability are hindered by limited accessibility and incompetence [17,18]. Zeolites and niobic acid catalysts are less active than the amberlyst [19]. On those lines, promoted metal oxides offer several advantages over the aforesaid catalysts since they are stable, regenerable and active over a wide range of temperatures. The present study was undertaken against the above background. In this study various zirconia-based catalysts namely, ZrO₂, TiO₂-ZrO₂, WO_x/TiO₂-ZrO₂ and MoO_x/TiO₂-ZrO₂ were synthesized and investigated for esterification of glycerol with acetic acid. The prepared catalysts were characterized by means of BET surface area, X-ray diffraction, Raman spectroscopy and NH₃-temperature programmed desorption techniques. The influence of reaction parameters such as temperature, molar ratio of acetic acid to glycerol, catalyst wt.% (w.r.t. glycerol) and time-on-stream on the activity and selectivity are also investigated.

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2. Experimental

2.1. Preparation of catalysts

 ZrO_2 was prepared from an aqueous solution of $ZrOCl_2$ by adding dilute NH₄OH drop-wise up to pH 8. The obtained precipitate was washed several times with deionised water until free from chloride ions, dried at 393 K for 12 h and calcined at 923 K for 5 h. The TiO₂–ZrO₂ (1:1 mole ratio based on oxides), WO₃/TiO₂–ZrO₂ and MoO₃/TiO₂–ZrO₂ catalysts (10 wt.% WO₃ or MoO₃) were prepared by using coprecipitation and impregnation methods as described elsewhere [20]. The resulting samples were oven dried at 393 K for 12 h and calcined at 923 K for 5 h in air atmosphere. The investigated ZrO₂, TiO₂–ZrO₂ and MoO₃/TiO₂–ZrO₂ catalysts are referred to as Z, TZ, WTZ and MTZ, respectively.

2.2. Catalyst characterization

X-ray powder diffraction patterns have been recorded on a Siemens D-5000 instrument by using Cu K α radiation source and scintillation counter detector. The specific surface areas of the samples were determined on a Micromeritics Gemini 2360 instrument by N₂ physisorption at liquid nitrogen temperature. The NH₃-temperature-programmed desorption (TPD) measurements were performed on an AutoChem 2910 instrument (Micromeritics, USA) [20]. Raman spectra were obtained on a DILOR XY spectrometer equipped with a CCD detector.

2.3. Activity measurements

The catalytic activity for acetylation of glycerol was carried at atmospheric pressure in the temperature range of 313-393 K. In a typical experiment, 2 g of glycerol and 3.9-7.8 mL of acetic acid were taken in a 100 mL two necked round bottom flask with 0.1 g of catalyst. A Dean-Stark trap is attached to this round bottom flask to remove water from the reaction mixture during the reaction because water is a byproduct in the glycerol esterification reaction, which favors the deactivation of catalyst and reversibility of the reaction. Catalysts were pre-activated at 423 K for 2 h before catalytic runs. Samples were taken periodically and analysed by GC equipped with BP-20 (wax) capillary column and a flame ionization detector. The conversion and product selectivity were calculated as per the procedure described elsewhere [21]. For time-on-stream measurements, the reaction was performed from 0.5 to 70 h using a fresh catalyst. For catalyst reusablity, the wet catalyst after separating from the reaction mixture was used and there was no appreciable change in the catalytic activity up to 5 recycles.

3. Results and discussion

3.1. Catalyst characterization

Table 1 represents the BET surface area, amount of NH_3 desorbed and XRD phases of Z, TZ, WTZ and MTZ catalysts. As can be noted from this table, the promoted TZ samples exhibit less specific surface area than Z and TZ catalysts. This may be due to the formation of some non-

Table 1	
BET surface area, XRD phases and total acid	lity of Z, TZ, WTZ and MTZ Catalysts.

S. no.	Catalyst	BET SA (m ² /g)	XRD phases	NH ₃ desorbed (mmol/g)
1	Z	42	m-ZrO ₂ , t-ZrO ₂	0.21
2	TZ	30	ZrTiO ₄	0.26
3	WTZ	14	ZrTiO ₄ , Zr(MoO ₄) ₂	0.70
4	MTZ	7	ZrTiO ₄ , Zr(WO ₄) ₂	0.61

porous $Zr(MoO_4)_2$ and $Zr(WO_4)_2$ compounds in the case of promoted catalysts as reported earlier [20]. In the XRD patterns of Z, we observed characteristic peaks at $2\theta = 28.3$, 24.46 and 31.58° correspond to the monoclinic-ZrO₂ phase and lines at $2\theta = 30.27$ and 49.21° due to tetragonal-ZrO₂ phase (monoclinic-ZrO₂ phase dominating over the tetragonal-ZrO₂ phase). While the formation of crystalline ZrTiO₄ compound was noted in the case of TZ and promoted TZ samples. In the case of MTZ and WTZ catalysts, we also observed the formation of $Zr(MoO_4)_2$ and $Zr(WO_4)_2$ compounds respectively, in addition to the ZrTiO₄ compound. We did not observe any peaks due to crystalline MoO₃ and WO₃ which suggest that a strong interaction exists between the dispersed MoO_x or WO_x and the support. The number of acidic sites of the pure support normally changes up on incorporation of promoters. In case of WTZ and MTZ catalysts, the concentration of acidic sites increased significantly when compared to that of pure TZ support. The number of acidic sites on the WTZ catalyst are higher than that of the MTZ catalyst.

The Raman spectra of Z, TZ, WTZ and MTZ catalysts are shown in Fig. 1. The Raman spectra of Z sample exhibited bands corresponding to a mixture of monoclinic- ZrO_2 (180, 188, 331, 380, and 476 cm⁻ and tetragonal- ZrO_2 (290, 311, 454 and 647 cm⁻¹) phases [22] and the monoclinic ZrO₂ phase dominating over the tetragonal ZrO₂ phase as observed from XRD measurements. The TZ and promoted TZ catalysts exhibited Raman bands at 168, 280, 338, 412, 640 and 803 cm⁻¹ which must be attributed to ZrTiO₄ compound. Raman bands at high frequency region $(700-1100 \text{ m}^{-1})$ of the WTZ catalyst are due to the presence of geometrically different WO_x species on the surface of the mixed oxide support [20,23]. These compounds may obstruct some of the active sites on the catalyst surface. This may be the reason why WTZ catalyst shows comparatively less activity than MTZ catalyst. Moreover, absence of bands due to crystalline MoO₃ and WO₃ obviously reveal that these have strongly interacted with the support as observed from XRD study. Nevertheless, the MoO₃ and WO₃ promoters enhanced the acidity of TiO₂-ZrO₂ mixed oxide and improved catalytic properties for the title reaction.

3.2. Catalytic experiments

The reaction products obtained in the acetylation of glycerol are monoacetin, diacetin and triacetin. Fig. 2 shows the glycerol conversion



Fig. 1. Raman spectra of Z, TZ, WTZ and MTZ catalysts.



Fig. 2. Acetylation of glycerol over (A) Z, (B) TZ, (C) WTZ and (D) MTZ catalysts. Reaction conditions: molar ratio of acetic acid to glycerol = 6:1; catalyst amount = 5 wt.% (w.r.t. glycerol); reaction temperature = 393 K. - Glycerol conversion; _____ Monoacetin; - Diacetin; - Triacetin.

and the selectivity of the products over Z, TZ, WTZ and MTZ catalysts at 393 K during 3 h of catalytic run and the products analyzed at different time intervals. It was observed that all catalysts exhibit excellent catalytic activity and generate the products within a short reaction time. The conversion of glycerol and selectivity towards di- and triacetin increased with reaction time, where as the selectivity of monoacetin decreased, because the di- and triacetin products are formed through consecutive esterification reactions [12]. In comparison to the promoted TZ catalysts, the Z and unpromoted TZ catalysts exhibited less acivity due to weak acidic sites as discussed in the above paragraphs. The WTZ and MTZ catalysts exhibited comparable activity as there is a slight difference in the number of acidic sites between these catalysts, which can be corroborated with the TPD results. Among all catalysts, the MTZ catalyst exhibited the highest glycerol conversion of ~ 100%.

Table 2 shows the influence of temperature on the acetylation of glycerol over Z, TZ, WTZ and MTZ catalysts. It was observed that the conversion of glycerol and the selectivity towards di- and triacetin increased with reaction temperature where as the selectivity of monoacetin decreased. This observation suggests that product selectivity varies with glycerol conversion as well as temperature. At 393 K the glycerol conversion over WTZ and MTZ catalysts was ~99% and ~100% respectively, while it was ~87% and ~92% over Z and TZ catalysts respectively.

Table 3 shows the effect of mole ratio of acetic acid to glycerol on glycerol conversion and selectivity to mono-, di- and triacetin products over Z, TZ, WTZ and MTZ catalysts. The reaction was studied by varying the acetic acid to glycerol molar ratio from 3:1 to 6:1 at a reaction temperature of 393 K. It was observed that these catalysts

Table 2

Effect of temperature on acetylation of glycerol over Z, TZ, WTZ and MTZ catalysts. Reaction conditions: molar ratio of acetic acid to glycerol = 6:1; catalyst amount = 5 wt.% (w.r.t. glycerol); reaction time = 3 h.

Catalyst	Temperature (K)	Glycerol conversion (%)	Selectivity (%)		
			Monoacetin	Diacetin	Triacetin
Z	313	4.67	100	-	-
	353	30.96	95.44	4.52	-
	393	86.32	57.94	36.67	5.39
TZ	313	5.34	100	-	-
	353	38.72	92.27	7.73	-
	393	91.53	54.72	39.40	5.88
WTZ	313	12.61	100	-	-
	353	42.68	91.99	8.01	-
	393	99.02	53.21	40.01	6.78
MTZ	313	18.57	100	-	-
	353	50.72	88.87	11.13	-
	393	~100	52.03	40.45	7.52

Table 3

Effect of mole ratio of acetic acid to glycerol on acetylation of glycerol over Z, TZ, WTZ and MTZ catalysts. Reaction conditions: catalyst amount = 5 wt.% (w.r.t. glycerol); reaction temperature = 393 K; reaction time = 3 h.

Catalyst	Mole ratio (AcOH:Gly)	Glycerol conversion (%)	Selectivity (%)		
			Monoacetin	Diacetin	Triacetin
Z	3:1	78.57	74.57	22.61	2.82
	4:1	79.71	70.91	25.40	3.69
	5:1	82.28	64.91	30.75	4.34
	6:1	86.32	57.94	36.67	5.39
TZ	3:1	80.66	70.50	25.96	3.54
	4:1	83.48	68.24	27.59	4.17
	5:1	84.20	62.04	33.02	4.94
	6:1	91.53	54.72	39.40	5.88
WTZ	3:1	85.05	65.89	30.04	4.07
	4:1	87.24	63.87	31.16	4.97
	5:1	93.89	58.83	35.29	5.88
	6:1	99.02	53.21	40.01	6.78
MTZ	3:1	90.66	59.56	34.98	5.43
	4:1	92.68	55.81	37.07	6.23
	5:1	94.61	54.64	39.08	6.78
	6:1	~100	52.03	40.45	7.52

show better activity even at low acetic acid to glycerol molar ratio. Over the MTZ catalyst the glycerol conversion was ~91% at a molar ratio of 3:1 and selectivity to monoacetin, diacetin and triacetin were ~60%, ~35% and ~5%, respectively. Where as at 6:1 molar ratio the glycerol conversion was ~100% and the selectivity to monoacetin, diacetin and triacetin were ~52%, ~40% and ~8%, respectively. Based on these results it can be stated that the change in molar ratio of acetic acid to glycerol also influences the conversion of glycerol and selectivity of the products. Increase in acetic acid to glycerol molar ratio increases in the selectivities of di- and triacetin products and decreases the selectivity of monoacetin. Due to more concentration of acetic acid at higher acetic acid to glycerol molar ratios, the selectivity towards di- and triacetin are high and *vice-versa*.

Fig. 3 shows the time-on-stream studies up to 70 h over MTZ catalyst at a reaction temperature of 393 K. The reaction products were analyzed at different time intervals. At 60 h of reaction time, the MTZ catalyst showed a maximum selectivity of ~80% triacetin and then there is no big change in the selectivity of triacetin. It is interesting to notice that initially the selectivity towards monoacetin is high and as the reaction is proceeded the selectivity towards di- and triacetin increased during 15 h of reaction time, then the selectivity



Fig. 3. Effect of reaction time on acetylation of glycerol over MTZ catalyst. Reaction conditions: molar ratio of acetic acid to glycerol = 6:1; catalyst amount = 5 wt.% (w.r.t. glycerol); reaction temperature = 393 K. _____ Glycerol conversion; _____ Mono-acetin; ____ Diacetin; ____ Triacetin.



Fig. 4. Effect of catalyst wt.% on acetylation of glycerol over MTZ catalyst. Reaction conditions: molar ratio of acetic acid to glycerol = 6:1; reaction temperature = 393 K; reaction time = 3 h. _____ Glycerol conversion; _____ Monoacetin; _____ Diacetin; _____ Triacetin.

towards diacetin also decreased but selectivity towards triacetin increased. This is mainly due to further acetylation of mono- and diacetin to yield the stable triacetin product.

Fig. 4 shows the effect of catalyst wt.% on glycerol conversion and selectivity of products over MTZ catalyst at 393 K. The glycerol conversion and selectivity towards mono-, di- and triacetin were increased with increase in catalyst weight up to 5 wt.% due to the availability of more number of active sites. However, with further increase of catalyst wt.% there is no big change on the glycerol conversion and selectivities of the products [14].

4. Conclusions

The acetylation of glycerol with acetic acid was carried out over ZrO_2 , TiO_2-ZrO_2 , WO_3/TiO_2-ZrO_2 and MOO_3/TiO_2-ZrO_2 solid acid catalysts. The effect of various parameters such as reaction temperature, molar ratio of acetic acid to glycerol, catalyst wt.% and time-onstream were studied to optimize the reaction conditions. It was observed that the MOO_3/TiO_2-ZrO_2 catalyst exhibits best catalytic activity (~100% conversion) with a maximum selectivity of ~80% triacetin at 60 h of reaction time. The optimized reaction conditions for the MOO_3/TiO_2-ZrO_2 catalyst are observed to be 393 K reaction temperature, 6:1 acetic acid to glycerol ratio and 5 wt.% catalyst. The selectivity of triacetin in the acetylation of glycerol was observed to depend on reaction time, acetic acid concentration and the nature of catalyst.

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