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Synthesis of bio–additive fuels from acetalization of glycerol with benzaldehyde over molybdenum promoted green solid acid catalysts

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ABSTRACT

The heterogeneous green solid acid catalyzed acetalization of glycerol with various benzaldehydes was investigated under solvent-free conditions. The investigated catalysts namely ZrO_2 and TiO_2–ZrO_2, and the respective MoO_3 promoted catalysts were prepared by a facile precipitation and wet-impregnation method, respectively. The physicochemical characteristics were achieved using X-ray diffraction, BET surface area, ammonia–temperature programmed desorption, Raman spectroscopy and FT–infrared spectroscopy techniques. Characterization results revealed that addition of MoO_x enhances the surface acidic properties of the oxide supports. The MoO_x/TiO_2–ZrO_2 catalyst exhibited a superior 74% glycerol conversion with 51% 1,3-dioxane product selectivity. Various reaction parameters were investigated to enhance the glycerol conversion as well as product selectivity. Particularly, the reaction temperature showed a significant influence on the glycerol conversion, whereas the effect of solvents was negligible. The conversion of glycerol was considerably decreased with substituted benzaldehydes due to steric hindrance. On the other hand, a high selectivity (71%) of 1,3-dioxane was obtained in the case of *p*-anisaldehyde. These interesting results suggest that MoO_x/TiO_2–ZrO_2 is a highly promising green solid acid catalyst for environmentally benign synthesis of bio-additive fuels from glycerol.

1. Introduction

During the past few decades, fossil fuels have proven to be the main energy sources for the development of economy and society. Concurrently, they cause severe environmental and human health problems, such as global warming, acid rain, heart diseases, respiratory troubles, etc. Accordingly, a great deal of research efforts has been undertaken, of which utilization of biofuels as substitutes to fossil fuels has gained considerable attention in recent years. Among the biofuels, biodiesel is a primary alternative to the diesel fuel since it shows similar properties of diesel fuel and reduces emissions of CO, CO_2, sulfur, hydrocarbons and the particulate matter [1–3]. Predominantly, biodiesel can be produced by transesterification of vegetable oils with methanol under basic or acidic conditions. Glycerol is the main byproduct during biodiesel production with ~10 wt.% of the total biodiesel synthesized (Scheme 1) [4,5]. The global biodiesel market is growing remarkably at an average annual rate of 42% and expected to reach 37 billion gallons by 2016 [6]. Presently, the high cost of raw materials (e.g., virgin oil) used for the transesterification process is the major problem towards the commercialization of biodiesel production. The high price of virgin oil contributes potentially as much as 70% of the total cost of the biodiesel. The use of low quality oils, such as waste cooking oils and non-edible oils is one of the alternative ways to reduce the cost of raw materials. Low-quality oils are cheaply available and can be regarded as attractive feedstocks for biodiesel production. However, the presence of high percentages of large quantities of unsaponifiable matter, water and free fatty acids makes the low-cost oils incompatible for the industrial process based on alkaline catalysis [7,8]. Therefore, synthesis of industrially useful chemicals from biodiesel-derived glycerol will be the key factor to enhance the profitability of biodiesel production.

In 1860, Alfred Nobel found the first industrial application of glycerol, i.e., nitroglycerin, which later gave access to dynamite [9]. Afterward, various reaction methodologies for the conversion of glycerol to valuable chemicals, including oxidation, hydrogenolysis, dehydration, pyrolysis, steam reforming, etherification, esterification, acetalization, oligomerization, polymerization and others have been reported [10,11]. Amongst, the acetalization of glycerol is one of the most important processes for the synthesis of green and cost-effective bio-additive chemicals from glycerol. Glycerol reacts with simple carbonyl compounds to provide isomeric six- (1,3-dioxane) and five-membered (1,3–dioxolane) cyclic products as novel fine chemical intermediates. In the acetalization reaction, usually 50% of each 1,3-dioxane and 1,3-dioxolane could be obtained. By varying the reaction parameters, such as temperature and molar ratio of the carbonyl compound to glycerol, the selectivity of acetals could be changed [12]. Notably, the glycerol acetals and ketals are employed as additives for diesel fuels, as bases for surfactants and as scents or flavors in the food and cosmetic industries [13]. The addition of cyclic acetals to standard diesel fuel considerably reduces the emission of CO, hydrocarbons and unregulated aldehydes. Similarly, they can be

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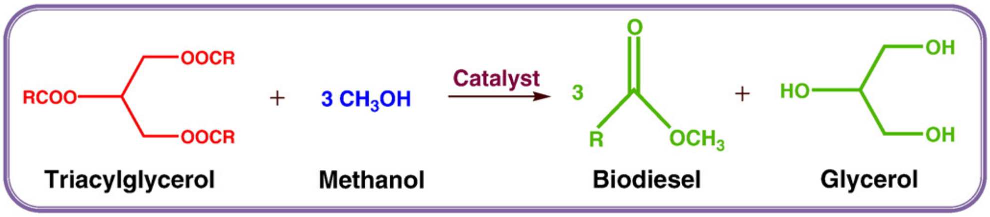

Scheme 1. Production of biodiesel through transesterification of triacylglycerol with methanol.

used as cold flow improvers for biodiesel [14]. Further, 1,3-dioxanes are potential precursors for the synthesis of green platform chemicals, such as 1,3-dihydroxyacetone and 1,3-propanediol [12].

Traditionally, the acetalization of glycerol is an acid catalyzed reaction and several homogeneous acids, such as HCl, H_3PO_4 and *p*-toluenesulfonic acid (PTSA) are used for acetalization of glycerol [12]. As well, the use of organic solvents, for example, benzene, chloroform and toluene to increase the glycerol conversion has been also described [14]. However, such procedures are environmentally unfriendly due to the application of toxic reagents, tedious work-up procedures and disposal of the effluents. Therefore, there is a tremendous effort to replace the liquid acids with solid acids [15]. In recent years, heterogeneous solid acid catalysts have gained remarkable curiosity because of their potential to replace the hazardous liquid acid catalysts in the industrial processes. Solid acids can be easily separated from the reaction mixture either by filtration or by centrifugation and do not require neutralization procedure [7]. Moreover, in the solid acids, the nature of active sites is well-known and can be defined either by the presence of surface protons (Brønsted acid sites) or by coordinately unsaturated cationic centers (Lewis acid sites) [16,17]. Among various solid acids, the MoO_x or WO_x promoted ZrO_2 catalysts are quite promising because they are environmentally benign, easy to prepare, exhibit better thermal stability and display strong surface acidity [18,19]. Further improvements, however, are still required to meet the increased practical demands. Use of zirconia-based mixed oxides and subsequent impregnation with molybdate ions is one of the efficient ways to enhance the catalytic performance. Usually, mixed oxides show superior physicochemical and acidic properties than the individual component oxides, hence exhibit better catalytic activity [20]. Therefore, much attention has been focused on the development of molybdenum oxide promoted zirconia-based metal oxide catalysts [16–19].

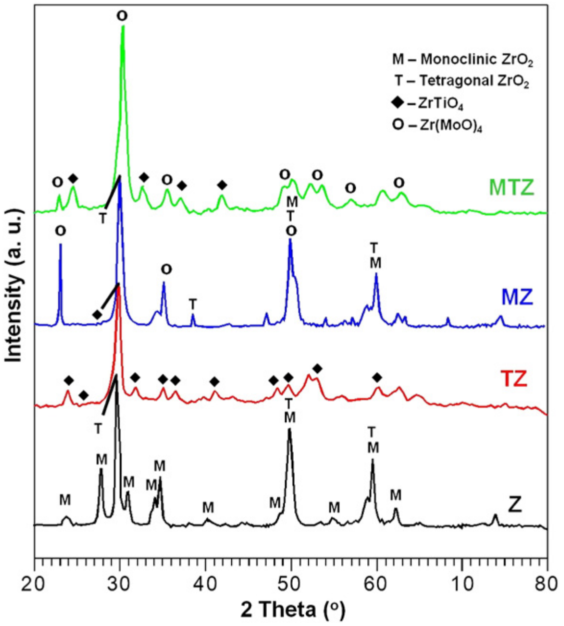

Fig. 1. X–ray diffraction patterns of ZrO_2 (Z), TiO_2–ZrO_2 (TZ), MoO_3/ZrO_2 (MZ) and MoO_x/TiO_2–ZrO_2 (MTZ) catalysts calcined at 923 K.

Accordingly, the present study was undertaken to synthesize alternative bio-additive fuels from acetalization of glycerol employing molybdenum oxide promoted acid catalysts. The investigated catalysts were characterized by means of BET surface area, X-ray diffraction, Raman spectroscopy, FTIR spectroscopy and NH_3–TPD techniques to examine the structural and surface acidic properties. The effect of various parameters, such as reaction temperature, molar ratio of glycerol to benzaldehyde, solvents, catalyst wt.% and time-on-stream was studied to enhance the glycerol conversion as well as product selectivity.

2. Experimental

2.1. Catalyst preparation

The investigated TiO_2–ZrO_2 mixed oxide (1:1 mole ratio based on metal oxides) was prepared by a facile coprecipitation technique from ultrahigh dilute aqueous solutions. In a typical procedure, the required amounts of $ZrOCl_2$ (Fluka, AR grade) and $TiCl_4$ (Fluka, AR grade) were dissolved in deionized water separately and mixed together under vigorous stirring. $TiCl_4$ was first digested in cold concentrated HCl and then diluted with double distilled water. Subsequently, aq. NH_3 solution was added drop-wise to the mixture solution until the pH of the solution reached ~8.5. The obtained precipitates were filtered off, washed several times until free from anion impurities and oven-dried at 393 K for 12 h. Some portions of the oven dried sample were calcined at 923 K for 5 h. Pure ZrO_2 was also prepared by adopting the same procedure under identical conditions.

The MoO_x/ZrO_2 and MoO_x/TiO_2–ZrO_2 catalysts containing 10 wt.% of MoO_3 were prepared by wet-impregnation method. In brief, the desired quantity of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich, AR grade) was dissolved in excess water followed by the addition of finely powdered oven dried zirconium or titanium–zirconium hydroxide/oxyhydroxide gel. The excess water was evaporated on a hot plate under vigorous stirring. The obtained products were oven dried at 393 K for 12 h and finally calcined at 923 K for 5 h. For convenience, the prepared ZrO_2, TiO_2–ZrO_2, MoO_x/ZrO_2 and MoO_x/TiO_2–ZrO_2 catalysts are referred to as Z, TZ, MZ and MTZ, respectively.

Table 1
BET surface area and total acidity of ZrO_2 (Z), TiO_2–ZrO_2 (TZ), MoO_x/ZrO_2 (MZ) and MoO_x/TiO_2–ZrO_2 (MTZ) catalysts calcined at 923 K.

S. No.	Catalyst	BET surface area (m^2/g)	NH_3 desorbed (mmol/g)
1	Z	42	0.21
2	TZ	30	0.26
3	MZ	94	0.47
4	MTZ	7	0.61