Valorization of Transesterification byproduct Glycerol to Solketal using Heterogeneous Catalyst

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by

Miss Sunita Maurya

Department of Chemistry Indian Institute of Technology

(Banaras Hindu University)

Varanasi 221005

India

Roll No. 19051009

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CHAPTER 7

Summary and Future prospectives

7.1 Summary of the thesis

This thesis is devoted to the catalytic activities of the transition metal-based mixed metal oxide catalysts towards the synthesis of solketal utilizing bio-waste glycerol as feedstock via the acetalization process. In this work, transition metal-based metal oxide was modified by incorporation of sulfonate group to improve the activity of the catalyst and used for designing heterogeneous catalysts. Different synthesis methods were adopted *viz*., wetness impregnation, coprecipitation method. There has been considerable improvement in the conversion and yield of glycerol and solketal, respectively, by using the synthesized heterogeneous catalysts. The synthesized catalysts like $SO_4^{-2}/ZrO_2-Al_2O_3$, $SO_4^{-2}/CoAl_2O_4-TiO_2$, and $SO_4^{-2}/ZnAl_2O_4-ZrO_2$ were found to be stable and show the catalytic activity was almost same up to six runs. The physicochemical properties of the synthesized catalysts support their good activity toward solketal synthesis. Green matrix studies were also carried out to ensure the environment-compatible nature of the acetalization process. Based on the work carried out, the following conclusions are explained.

Chapter 1 provides a concise overview of biodiesel as an alternative to fossil fuels, highlighting the production of glycerol as a byproduct of the biodiesel manufacturing process. It thoroughly explains the discovery, physical properties, and significance of glycerol.

Chapter 2 includes the literature survey of glycerol and its valorization to solketal using various types of homogeneous and heterogeneous acid catalysts. The reaction mechanism involved in the acetalization reaction of glycerol to solketal was also thoroughly explained in this chapter.

Chapter 3 describes the experimentation methods adopted for the synthesis of the designed catalysts. The chemicals used in designing catalysts and acetalization of glycerol were mentioned with specification and purity. Synthesis techniques like co-precipitation and wet-impregnation were adopted and broadly discussed. The physicochemical properties of the catalysts and the activity of the catalyst are studied by performing different characterization techniques. The techniques adopted and formulae used are explained in this chapter.

In Chapter 4, a systematic study of the catalytic activity of $SO_4^{-2}/ZrO_2-Al_2O_3$ catalyst towards solketal synthesis. The modified catalyst was synthesized by the simple wetness impregnation method, and the properties of the catalyst were studied by various techniques like TGA-DSC, XRD, FTIR, XPS, SEM-EDX, NH_3-TPD, and BET-surface area method. The synthesized catalyst was applied for the glycerol acetalization reaction. The activity of catalysts also depended on various properties of the catalyst, like crystallinity of catalyst, morphology of catalyst, and various reaction parameters like reaction temperature, glycerol to acetone molar ratio, reaction time, and catalyst dose, etc. Given the primary advantage of heterogeneous catalysts is their reusability, the study focused on evaluating this characteristic. It was observed that the catalyst remained stable through up to five cycles. The conversion percentage of glycerol was calculated using GCMS and NMR spectra.

In Chapter 5, $SO_4^{-2}/CoAl_2O_4-TiO_2$ catalyst was prepared by taking different stoichiometric mass ratios of $CoAl_2O_4$ and TiO_2 and was tested for acetalization of glycerol. Among all these synthesized catalysts, $SO_4^{-2}/CoAl_2O_4-TiO_2$ (3:2) was one of the best catalysts providing the highest conversion of glycerol, i.e., 99 %. The synthesized catalyst was utilized for the acetalization of glycerol with acetone and was found to be very efficient. The characterization results demonstrate that the incorporation of the sulfonate group of the $CoAl_2O_4-TiO_2$ lattice enhances the acidic strength of the modified catalyst, which potentially shows its activity toward solketal production. In this study, the optimum reaction conditions for acetalization of glycerol were 120 min reaction time, 58 °C reaction temperature, acetone to glycerol molar ratio 10:1, and catalyst dose 3 wt.% of glycerol used (in g). The catalyst was active up to the 6th catalytic cycle in the acetalization of glycerol. On the basis of the acidity test, it can be concluded that the acidity of the $SO_4^{-2}/CoAl_2O_4-TiO_2$ catalyst plays a major role in the conversion of glycerol to solketal, which shows remarkable performance in the acetalization reaction. The catalytic activity of prepared $SO_4^{-2}/CoAl_2O_4-TiO_2$ was evaluated through NMR and GCMS spectroscopic analysis of the synthesized product and disclosed a good efficiency in mild reaction conditions with 99 % conversion and 98 % yield.

In Chapter 6, the comparative studies on the effect of change in one active component on the activity of catalyst towards solketal synthesis have been established. For which, $ZnAl_2O_4$ was firstly synthesized by co-precipitation route and then modified with TiO_2 and ZrO_2 to increase the thermal stability, followed by the sulphonation to improve the acidity of the modified catalyst and applied in acetalization of glycerol. The physicochemical properties of the synthesized catalysts were investigated and compared by TGA, XRD, SEM-EDX, FTIR, XPS, BET-surface area, etc. The comparative study of the catalytic activity of $SO_4^{-2}/ZnAl_2O_4-ZrO_2$ (SZZ) and $SO_4^{-2}/ZnAl_2O_4-TiO_2$ (SZT) was performed for acetalization of glycerol via reflux condensation process. Among both SZZ and SZT catalysts, SZZ obtained the highest conversion of glycerol, i.e., 99.3 % with 98% solketal yield, whereas SZT provided only 83% glycerol conversion with 81 % solketal yield at the optimized reaction conditions. The reason behind the higher catalytic activity of SZZ than that of SZT was studied and proved. The lower surface area and acidity of SZT are mainly responsible for the poor glycerol conversion percentage. The catalyst reusability study suggested that SZZ possessed appreciable catalyzing potential and stability for six runs, giving 84 % conversion.

Chapter 7 of the thesis presents the overall summary, and future scope of the work carried out for the solketal synthesis process.

The correlation study of the activity of all the synthesized catalysts towards solketal synthesis revealed that the $SO_4^{-2}/ZnAl_2O_4\text{-}ZrO_2$ catalyst is one of the best catalysts, providing appreciable glycerol conversion of 99.3% with 98 % solketal yield. Also, the catalyst is reusable for up to six reaction cycles and shows a high turnover frequency, which signifies the potency of the SZZ catalyst.

7.2 Future scope of present work

The cost of producing biodiesel can only be decreased by effectively converting crude glycerol into certain value-added products. In order to address global energy and environmental concerns, the catalytic conversion of renewable biomass resources, such as glycerol, into value-added products became crucial. For society to flourish sustainably, it is crucial to convert renewable feedstock into various value-added chemicals. Glycerol may now be converted into valuable compounds by a number of innovative catalytic conversion techniques that have recently been discovered. Solketal is one of the most desirable compounds among numerous value-added products because of its excellent characteristics, including low toxicity, high solubility, good biodegradability, and low flammability. It can be utilized as a surfactant, disinfectant, flavoring agent in food and cosmetics, a plasticizer in polymer chemistry, as a solubilizing and suspending agent in the pharmaceuticals industry.

The current study uses the sulphonated transition metal-based heterogeneous acid catalyst to synthesize high-quality solketal from biowaste glycerol derived from biodiesel. The extended work of the present study may focus on the use of solketal as a green solvent in various chemical syntheses due to its low toxicity and biodegradability. Solketal can be used to modify drug molecules to improve their stability and delivery properties. Apart from this, solketal could be used as an oxygenate additive in biodiesel and gasoline to improve the fuel properties, including enhancing the octane number and cold flow property, increasing the oxidation stability, improving the flash point, and reducing the gum formation and environmental pollution. A suitable methodology can be developed and its further application can be carried out for future work.