

Green synthesis of cyclohexanone glycerol ketal catalyzed by a solid superacid

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Abstract This paper discusses the synthesis of a glycerol ketal compound obtained from condensation reaction of cyclohexanone with glycerol catalyzed by a solid superacid. The solid superacid $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$ was prepared using coprecipitation and impregnation method and characterized by X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy and elemental analysis. The surface acidity was measured by thermogravimetric analysis of adsorbed n-butylamine. In order to achieve the optimal reaction conditions, five impact factors: molar ratio of glycerol to cyclohexanone, catalyst calcination temperature, reaction time, catalyst amount and molar ratio of Ti/La were investigated in the experiments. Synthesized ketal compounds were analyzed by GC-MS/MS. Under the best conditions, the cyclohexanone glycerol ketal yield could reach up to 97%.

Keywords: glycerol, solid superacid, cyclohexanone, ketals

1. Introduction

Glycerol is a 10% by-product of biodiesel production leading to an alarming increase of crude glycerin in the market with currently 350,000 tons per annum (tpa) production in the USA and 600,000 tpa in Europe [1] which will still increase due the new energy legislation implemented in Europe states that by the end of 2020 traffic fuels should contain 10% in energy content produced from renewable sources. Therefore, it is important to find new applications for the excess of glycerin produced from biodiesel.

The chemical transformation of glycerin into more economic valuable products has attracted the attention of the scientific community in recent years. Among the possible glycerol derivatives, which find applications in fuel, plastic and fine chemical industries, can be quote ethers, esters, diols and acetals/ketals compounds [2]. There is considerable interest in synthesizing acetals and ketals as important perfume substances and industrial raw materials of organic synthesis [3]. Concentrated sulfuric acid and other analogous Brønsted acids used as catalysts in industrial processes for many years, exposed their defects, such as the corrosion of

the reactors, difficulties in product separation and catalyst recovery, pollution by acidic waste water, poor quality of the products, etc.

Catalysts based on solid superacid have many advantages over liquid acid catalysts. They are non-corrosive, environmentally friendly and present fewer disposal problems. Their repeated use is possible and separation from liquid products is easier compared to homogeneous catalysts [4]. Solid superacid has excellent catalytic activity for esterification due to its super acidity in heterogeneous systems. This type of catalyst was successful used in several important acid-catalyzed reactions (esterification, acylation) [5, 6].

This paper presents our results related to obtaining cyclohexanone glycerol ketal from glycerol and cyclohexanone, in presence of a green catalyst $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$.

2. Experimental

2.1 Catalyst preparation

$\text{TiO}_2\text{-La}_2\text{O}_3$ mixed oxide with different molar ratio Ti/La (40:1; 30:1; 20:1 and 10:1) were obtained by co-precipitation method. Cold aqueous solution

of TiCl_4 was slowly added to aqueous solution of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$. To this mixture, 3M aqueous NaOH was added dropwise under vigorously stirring until pH reaches 8,5. The obtained precipitate was filtrated, washed several times with deionised water until the Cl^- in the filtrate could not be identified. The cake was dried at 110°C for 12 h. The powder was impregnated in a 1 M H_2SO_4 (7,5 ml/g catalyst) and sonificated 10 minutes under vacuum, followed by filtration, drying and calcination at 480°C for 3h.

2.2 Catalyst characterization

The XRD measurements were carried out using a Bruker D8 Advance, X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$) operating at a voltage of 40 kV and a current of 40 mA. Data were collected in 2θ range from 10° to 70° , with a scanning rate of 0.1 deg.min^{-1} . The FT-IR measurements were performed with a Tensor 27 FT-IR Spectrometer Bruker, employing KBr pellet technique. Thermogravimetric analysis of the compounds were recorded in a TGA/SDTA 851 Mettler Toledo in the temperature range $20\text{--}700^\circ\text{C}$. Elemental analysis were carried out using a 2400 Series II CHNS/O Perkin Elmer Analyzer.

The total acidity of the solid samples was measured by thermogravimetric analysis of adsorbed n-butylamine.

2.3 Typical reaction procedure

The reaction was carried out in a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and Dean&Stark separator to remove the water formed along the reaction process (toluen was chosen to make the azeotrope with water). In a typical experiment, glycerol and catalyst were placed under reaction conditions for 10 min before cyclohexanone was added dropwise. The reaction mixture was mechanical stirred at atmospheric pressure and heated to reflux. After the reaction was completed the sample was filtrated and submitted to distillation to remove solvent and excess of cyclohexanone.

The products were confirmed by GC-MS/MS (model GC-MS/MS Agilent 7890 A, Network GC Sistem equipped with a Quadrupole mass spectrometer detector type 5975 HP / N 5989-

6427EN inert XL EI / CI MSD with triple axis G3174A detector).

3. Results and Discussions

3.1 XRD characterizations

The X-ray powder diffraction spectrum of solid samples $\text{SO}_4^{2-}/\text{TiO}_2\text{--La}_2\text{O}_3$ and $\text{SO}_4^{2-}/\text{TiO}_2$ are shown in **Fig. 1**. The diffractograms showed that the samples used in this study were all present in anatase phase and well crystallized (JCPDS, No. 21-1272). No rutile phase was detected in these oxides, all these indicating that calcination at 480°C was suitable. Moreover, no diffraction peak due to La_2O_3 was found, suggesting that no sole crystalline phase caused La_2O_3 and La is dispersed on the catalyst surface in case the amount of La is below a threshold value [7].

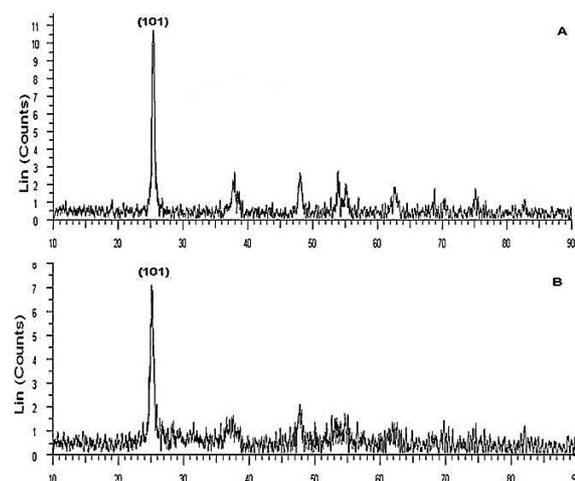


Fig.1. XRD measurements of A: $\text{SO}_4^{2-}/\text{TiO}_2$ and B: $\text{SO}_4^{2-}/\text{TiO}_2\text{--La}_2\text{O}_3$

3.2 Infrared spectra

The FT-IR spectrum of $\text{SO}_4^{2-}/\text{TiO}_2\text{--La}_2\text{O}_3$ is presented in **Fig. 2**. Infrared spectrum of solid sample exhibit a sharp band at 1374 cm^{-1} attributed to the stretching frequency of the free sulfate groups [8]. Moreover, the spectrum contained three shoulders at around 1199 , 1139 and 1052 cm^{-1} which were the characteristic frequencies of a bidentate SO_4^{2-} coordinated to metals such as Ti [9]. Such structures could strongly withdraw electrons from

the neighboring Ti cations, resulting in lots of electron-deficient metal centers on the Ti cations that acted as strong Lewis acid sites. This can be the source in the generation of a large amount of surface acidic sites on solid acids of sulfated metal oxides [10]. The presence of sulphate anions on the catalyst surface is supported by elemental analysis which indicated 4,3 % sulf.

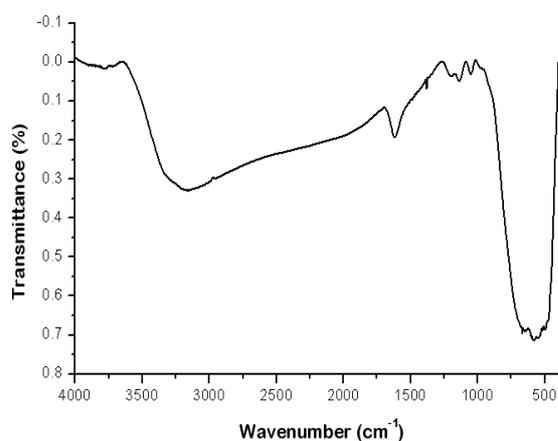


Fig. 2 FT-IR spectra of $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$

3.3 Thermal analysis

The thermogravimetric analysis of solid superacid $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$ is shown in Fig 3.

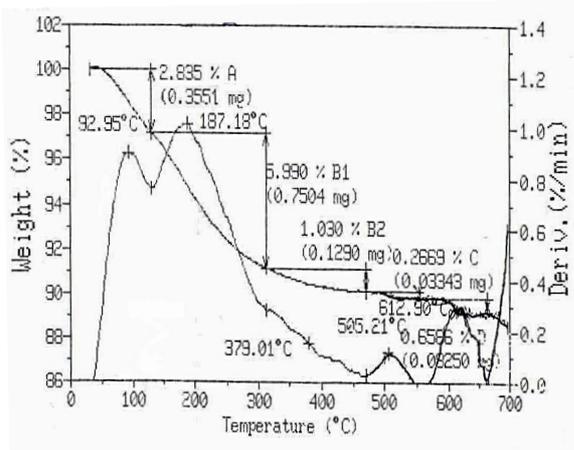


Fig. 3 TGA of $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$

The sample exhibited 3 different ranges of weight loss, from 30 to 200°C, from 200 to 500°C

and from 500°C to higher temperature. A first weight loss was observed from about 50 to 190°C and is caused by the elimination of physically adsorbed water in the pores and on the surface, while the second mass loss from 200 to 500°C is due to the loss of chemically bonded water. The last two peaks from the temperature region over 500°C are caused by the decomposition of surface sulfate anions [11].

3.4 Acidity measurements - TGA of chemisorbed n-butylamine

The total acidity defined as the absolute mass of base desorbed from the acid sites of the catalyst, expressed in acid sites per g, was estimated by thermogravimetric analysis (TGA) of adsorbed n-butylamine (Fig.4.)

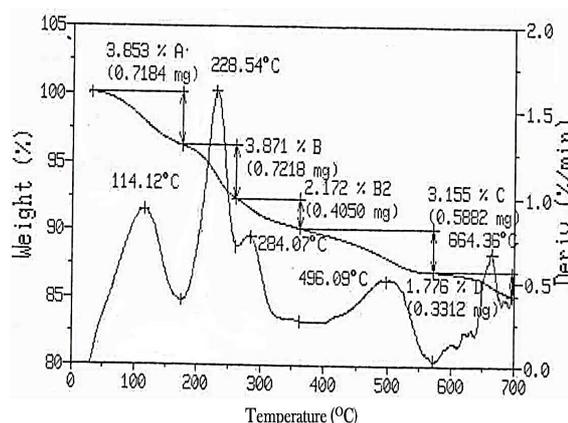


Fig. 4 TGA of chemisorbed n-butylamine

The TGA data shows that catalyst has 0.29 meq/g of medium acid site exhibited by the peak dissociation of the n-butylamine at 243-403°C and 0.67 meq/g strong acid sites, determined by the dissociation peak of the n-butylamine at 403-664°C.

3.5 Optimization of reaction conditions

The solid superacid was used to catalyze the ketalization of glycerol with cyclohexanone. In order to achieve the optimal reaction conditions, five impact factors, such as molar ratio of glycerol to cyclohexanone, catalyst calcination temperature, reaction time, catalyst amount and molar ratio of Ti/La were investigated in the experiments

(Fig. 5-10). The results clearly show that conversion increased with time (Fig.5).

The reaction occurred very quickly at first with the conversion over 66,47% after 5 minutes of

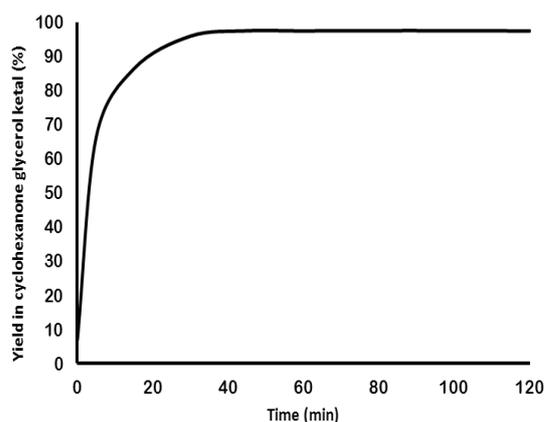


Fig.5 Influence of reaction time on the reaction performance

reaction. After 30 min of reaction, the cyclohexanone glycerol ketal conversion was 95.95%. It is interesting to notice that the ketal conversion is around 85% even after 15 min of reaction, indicating the high activity of the solid superacid catalyst. Moreover the conversion rich the maxim value of 97.62 % after 45 min.

Another parameter investigated was the influence of molar ratio of glycerol to cyclohexanone.

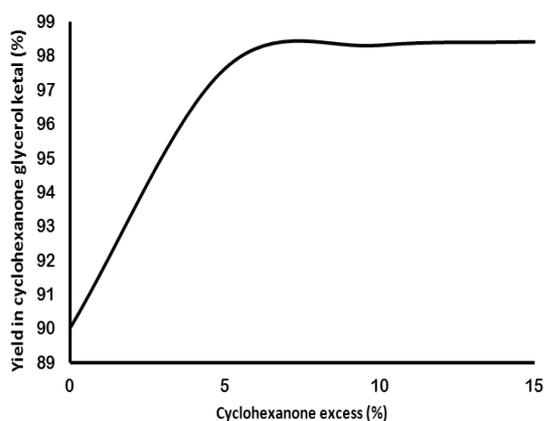


Fig. 6 Influence of cyclohexanone excess on the reaction performance

The date obtained (fig. 6) shows that yield in cyclohexanone glycerol ketal increase with the increasing of ketone excess. Increase in ketal yield is not significant for cyclohexanone excess higher than 0,05 mol/mol, so optimal molar ratio of glycerol to cyclohexanone was choose to be 1:1.05.

Figure 7 shows the influence of the catalyst amount on the reaction performances. As can be seen, there is a strong dependence between ketal yield and the amount of catalyst. Maximum yield in cyclohexanone glycerol ketal was achieved when 1.5 wt % of catalyst with respect to glycerol was used. Further increase of catalyst amount did not significant raise the yield.

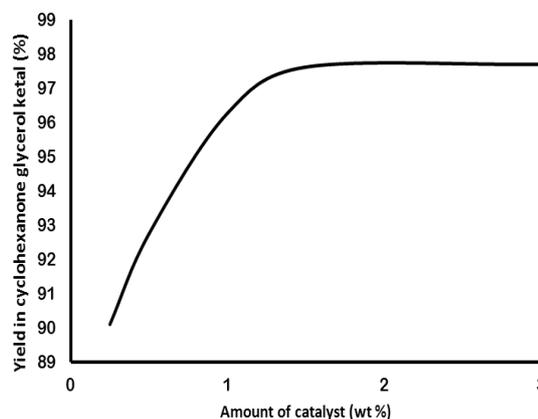


Fig. 7. Influence of amount of catalyst on the catalytic reaction performance

The preparation conditions of catalyst are important factors that can affect the solid superacid $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$ catalytic properties. The results presented in **Fig. 8** and **Fig. 9** show the calcination temperature and the mole ratio of Ti/La on the catalytic activity.

The calcination temperature is a very important parameter because it can affect not only the sulfate amount added to the catalyst surface but also the activity of the catalysts as well. The results showed (Fig. 8) that the catalytic activity of solid superacid calcined at about 480°C for 3 h is higher than that calcined at other temperatures, and that above 480°C this sulphate complex gradually decomposes. The value of calcination temperature is supported by the thermogravimetric analysis which exhibit two

peaks from the temperature region over 500°C that are caused by the decomposition of surface sulfate anions.

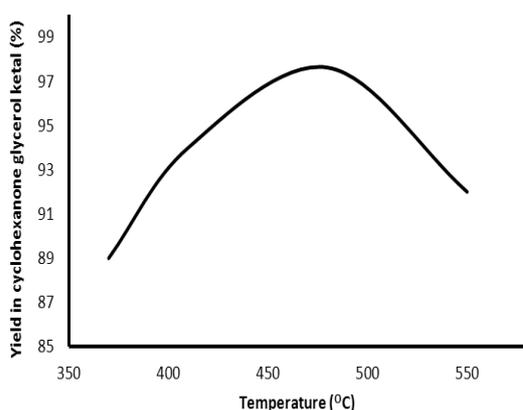


Fig. 8 Influence of calcination temperature on the catalytic activity

Regarding the influence of molar ratio the results showed (Fig. 9) that the $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$ optimal catalytic activity was obtained at mole ratio of $\text{Ti/La} = 30:1$.

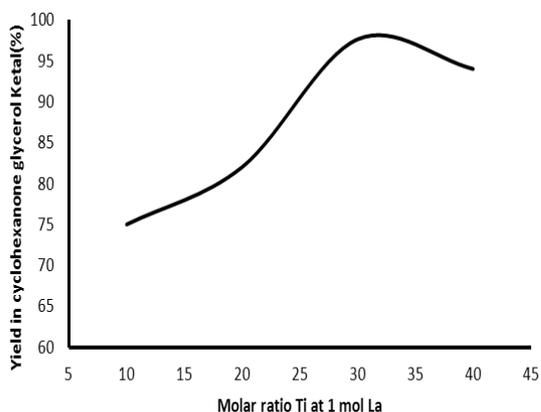


Fig. 9 Influence of molar ratio La:Ti on the catalytic activity

4. Conclusions

Efficient and environmental friendly procedure for the synthesis of cyclohexanone glycerol ketal catalyzed by solid superacid was investigated. $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$ was prepared by coprecipitation method and impregnating with sulfuric acid.

The characterization techniques of solid superacid indicates that $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$ is an heterogeneous catalyst with high activity, stability and acid strength. The experimental results show that maximum yield in cyclohexanone glycerol ketal of 97.62 % was reached at molar ratio ketone to glycerol of 1.05:1, the mass ratio of the catalyst used 1.5 wt % with respect to glycerol, the reaction time 1.0 h, catalyst calcination temperature 480°C for 3 h and the molar ratio $\text{Ti/La}=30:1$.

6. References

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