

Research Article

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Solid Acid Catalyzed Etherification of Glycerol to Potential Fuel Additives



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Abstract

Various acidic clay catalysts were evaluated for the etherification of glycerol with t-butanol (TBA). Complete glycerol conversion to MTBGE, DTBGE and TTBGE was achieved at 110 °C with 1:20 molar ratio of glycerol to TBA over Mont-KSF/O catalyst. The effects of various reaction parameters such as temperature, time, and catalyst loading and molar ratio of glycerol to TBA were studied. X-ray diffraction, scanning electron microscopy/energy dispersive X-ray spectroscopy, Thermo gravimetric analysis, Ammonia-Temperature programmed desorption, BET surface area measurement were performed to study various properties of the catalysts. NH₃-TPD revealed that Mont-KSF/O possessed highest acidity, thus it is active for etherification of glycerol. Mont-KSF/O could be successfully recycled for several times without losing its activity.

Keywords: Montmorillonite clay; Etherification; Oxygenated fuel additives; Dtbge; Tba

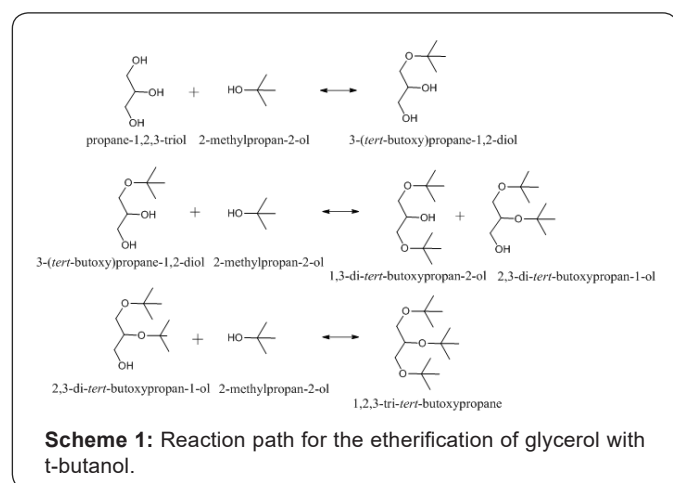
Abbreviations: MTBE: Methyl Tert-Butyl Ether; ETBE: Ethyl Tert-Butyl Ether; TAME: Tert-Amyl Methyl Ether; TEL: Tetra Ethyl Lead; EPA: Environmental Protection Agency; DTBGE: Di T-Butyl Glycerol Ether

Introduction

Eco friendly, non-toxic and renewable sources of fuels usually referred to as fatty acid esters are mainly produced by trans-etherification of triglycerides of vegetable oil or animal fat with low carbon footprint are emerging as alternative to petroleum fuels. These fuels can be biogenic which would reduce economic and environmental pressure with improvement in air quality, a cheaper product or better fuel properties [1-7] Worldwide use of biofuels is rapidly increasing which would reach to 20% by use of biodiesel on-road by 2020 [8]. As glycerol is the main byproduct of biodiesel production [9-12], the growth of biodiesel industries will result in over production of glycerol. Hence, there is a need to convert it into value added chemicals by adequate technologies [13-14]. Usually, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) were used as additives for diesel. These additives derived from non-renewable petroleum fossil fuels are costly and cause environmental pollution, so bio-derived fuel additives serving alternative to the petroleum fuel additives. Usage of lead was banned in 1995 (United States),

and then methyl tert-butyl ether (MTBE) was used as an additive in place of tetra ethyl lead (TEL). MTBE reduces the carbon monoxide emission from fuel but it is highly soluble in water and can contaminate drinking water. MTBE is causing carcinogenic effects on animals which were also banned in 2001 by Environmental Protection Agency (EPA) at United States [15]. Addition of glycerol ethers to diesel improves the combustion efficiency of thermal combustion engine. These ethers are useful as diesel additives due to their good blending property, high Cetane number, reduction in carbon monoxide and particulate matter emission from incomplete combustion on addition into fuel [16-17]. Glycerol cannot be added directly to diesel fuels because of its low solubility, poor thermal stability, its decomposition and polymerization at high temperature [18]. Conversion of glycerol to mono-, di- and tri-tert-butyl ethers by etherification is one of the promising processes among different strategies for valorization of glycerol [19] This has been also studied by several researchers with or without solvent and catalyzed by either homogeneous

or heterogeneous catalysts [20]. Glycerol etherification has been reported with isobutylene [21,22] and tert-butyl alcohol [23,24]. Mass transfer between glycerol and solvent strongly affects the performance of etherification process. From this perspective, tert-butyl alcohol is a useful reactant in the etherification reaction due to its high miscibility with glycerol [25]. While isobutylene having very low solubility, very expensive and requires high pressure to keep in liquid form [16] which increases handling problems. Etherification of glycerol is an acid catalyzed reaction (Scheme 1) to produce the mixture of alkyl glycerol ethers such as mono t-butyl glycerol ether (MTBGE), di t-butyl glycerol ether (DTBGE) and tri t-butyl glycerol ether (TTBGE). MTBGE has a low solubility in diesel fuel and therefore etherification of glycerol must be directed to the maximum formation of DTBGE and TTBGE. Etherification of glycerol was initially attempted with conventional mineral acids which limit the application of the process due to cumbersome work up procedures and added pollutant salts in the environments [16]. Among the solid acid catalysts, amberlyst-15 was well studied for the etherification of glycerol using isobutylene gas. After that t-butanol was explored as a safe and in dual role as reagent as well as solvent for the etherification due to easy and stable carbonation formation in acidic medium.



In continuation of our interest in bio-glycerol conversions to value added products, we explored here the use of commercially available montmorillonite clays as efficient solid acid catalysts for etherification of glycerol with t-butanol. Different montmorillonite clay catalysts were screened for the etherification of glycerol and conditions were optimized by studying the parameters effect over KSF/O catalyst.

Experimental

Materials

Montmorillonite KSF/O and other montmorillonite catalysts were purchased from fluka, India. Glycerol (99.5%) and t-butanol (99.7%) were supplied by Ajax Chemicals (India). Mont K10 was purchased from Sigma-Aldrich, Bangalore, India.

Experiment procedure

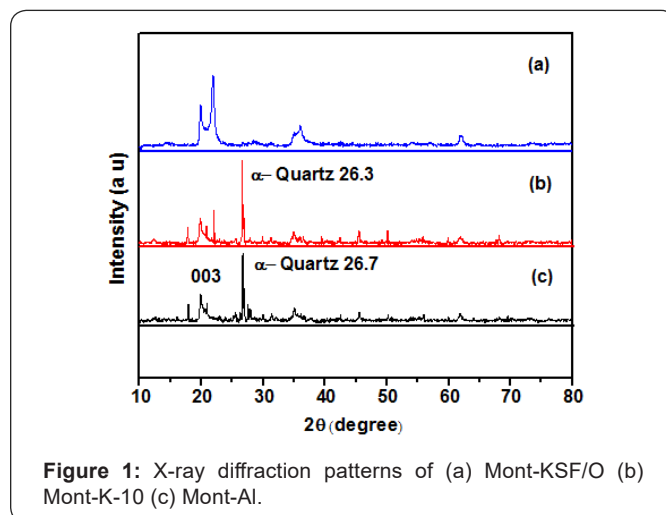
In a 100ml round bottom flask fitted with reflux condenser, glycerol (0.92g) and t-butanol (14.82g) were added and heated up to desired temperature for 10 min to withdraw initial sample. Then catalyst (0.250 g) was added and the mixture was heated at 110 °C for 6h. Then mixture was cooled down to 25 °C. Reaction progress was monitored by withdrawing samples in specific time interval and analyzed by injecting to gas chromatography (Shimadzu) equipped with HP INNOWAX capillary column and FID detector. GC conditions: Injection temperature; 300 °C, column temperature; 40 to 240 °C, detector temperature; 150 °C and carrier gas (N_2 ; 30 bar).

Catalyst Characterization Methods

Wide angle X-ray diffraction patterns (WAXRD) were recorded on a Analytical PXRD model X-Pert Pro-1712, using Ni filtered Cu-K α radiation ($\lambda = 0.154\text{nm}$) as a source (current intensity, 30mA; voltage, 40 kV) and a Accelerator detector. Surface area and acidity measurement (NH₃-TPD) of different montmorillonite clay catalysts was carried out using Micromeritics chemisorbed 2120 instrument. Pore size analysis of montmorillonite clay catalysts was carried out by Thermo Education Corporation, Italy, and PASAL 440 type instrument. The morphology of the catalyst was studied by SEM, JSM-6390 LV, Jeol, Japan and weight loss of the catalyst with temperature to 700 oC were observed by DTG-60, (Shimadzu) Japan, and TGA instrument.

Results and Discussion

Catalyst characterization

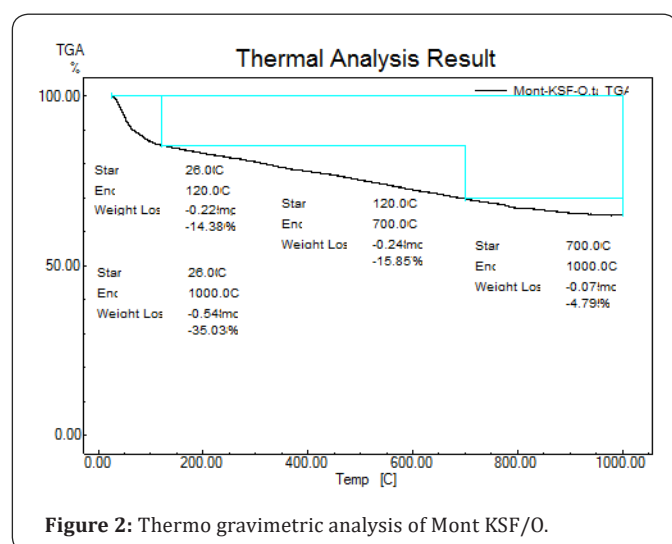


X-ray diffraction: The XRD patterns of KSF/O and Mont-K-10 in Fig.1 showed typical Q-quartz phases at 2θ , 26.7 and 26.3 °C containing the silica-aluminate crystalline layered structure. But in case of montmorillonite pillared Al, crystalline phase was totally absent which clearly indicated amorphous nature of montmorillonite pillared Al (Figure 1) [26,27].

Table 1: Surface area and acidity characteristics of different clay catalysts.

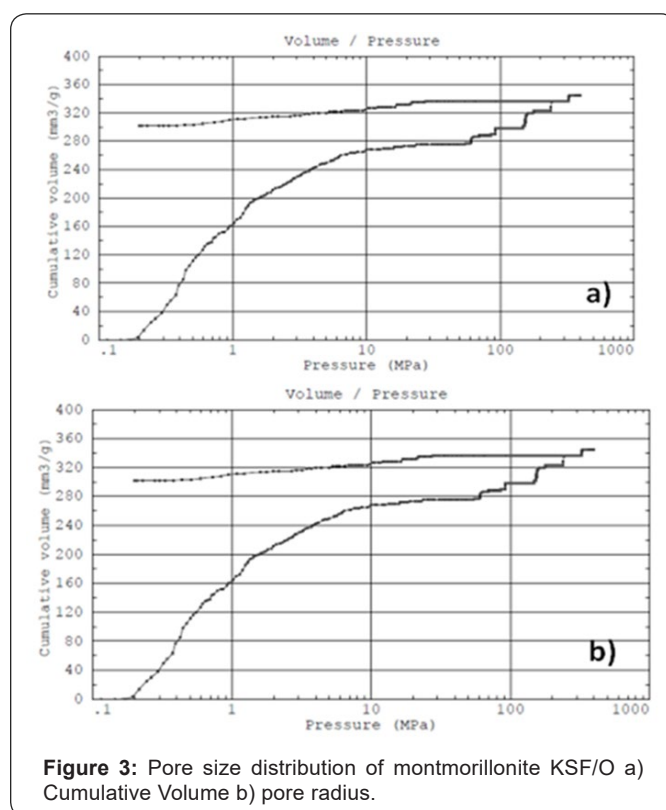
Catalysts	SBET, (m ² /g)	NH ₃ Adsorbed (mmol/g)	Distribution of Acidic Sites %	
			LT-Peak(150 °C)	HT-Peak(400 °C)
Montmorillonite KSF/O	128	0.015	25	75
Montmorillonite K-10	230	0.008	52	48
Montmorillonite Al	250	0.005	25	75

Physico-chemical characterization: Table 1 presents BET surface area and the surface acidity of various montmorillonite clay catalysts. Among all the catalysts, Mont-Al showed the highest surface area of 250m²/g and the order of surface area values were found to be Mont-Al > Mont- K-10 > Mont- KSF/O. The amount of total acid sites were determined by using NH₃-TPD and the order of acidity was Mont-Al (0.005 mmol g⁻¹) < Mont- K-10 (0.008 mmol g⁻¹) < Mont- KSF/O (0.015mmol g⁻¹).

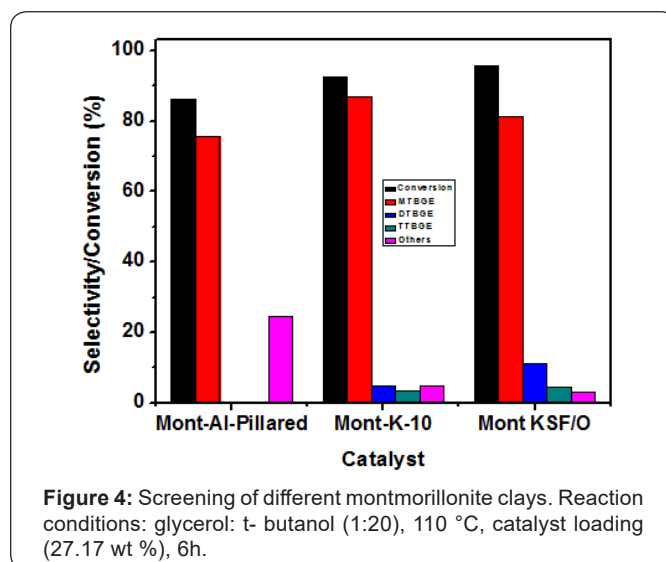
**Figure 2:** Thermo gravimetric analysis of Mont KSF/O.

Thermo gravimetric analysis: The weight loss during thermo gravimetric analysis was calculated from the ratio of change in weight to the initial weight of the sample. Due to the moisture loss, sudden drop in weight was observed for sample till 120 °C (Figure 2). Comparatively lower weight loss was observed in the range of 120 to 700 °C. It indicates that catalyst was quiet stable up to 700 °C.

Pore size distribution: The pore size distribution of montmorillonite KSF/O showed macro porous structure with an average pore radius of 616.043 nm and total cumulative volume of 345mm³/g (Figure 3). The pore size distribution of traditionally synthesized montmorillonite KSF/O was broader with a relative pore volume around 87%. Pore size analysis result shows the specific surface area of montmorillonite clay is about 32.96m²/g and porosity of 6.44%.

**Figure 3:** Pore size distribution of montmorillonite KSF/O a) Cumulative Volume b) pore radius.

Catalyst screening

**Figure 4:** Screening of different montmorillonite clays. Reaction conditions: glycerol: t- butanol (1:20), 110 °C, catalyst loading (27.17 wt %), 6h.

Etherification of glycerol with t-butanol was studied over three different montmorillonite clay samples at 110 °C using glycerol: t- butanol mole ratio of 1:20 with the catalyst loading of 27.17 wt% for duration of 6 h. The performance of the catalyst was measured in terms of glycerol conversion and the selectivity to di- and tri- ethers. Mont-KSF/O catalyst showed the highest glycerol conversion due to the Brønsted acidic sites having acidity of 0.015mmol g⁻¹ despite its lower surface area (128m²/g) as compared with other catalysts. In all the cases

MTBGE and DTBGE selectivity's were higher as compared to TTBGE (Figure 4). The Brønsted acid sites played an important role in the etherification of glycerol. The low conversion and selectivity with Mont-Al was due to its low ($0.008\text{mmol g}^{-1} \text{NH}_3$). The increase in conversion of glycerol to 100 % with Mont-KSF/O catalysts was due to their higher acidity (0.015mmol g^{-1}). Although the surface area values for montmorillonite Al and K-10 were higher, the acidity order makes montmorillonite KSF/O as a highly active catalyst for etherification (order of acidity montmorillonite KSF/O > K-10 > Mont-Al).

Influence of reaction time

Since glycerol etherification in t-butanol is a stepwise process initiating with the formation of mono-ether followed by the formation of di- and tri-ethers thus, study of conversion of glycerol and selectivity of products against time becomes a very important aspect. As can be seen them in (Figure 5), within first hour of the reaction time, glycerol was completely converted with the highest selectivity towards 87%, 9% and 3% of MTBGE, DTBGE and TTBGE, respectively. However, simultaneous decrease in the MTBGE and increase in DTBGE was observed after 12h (Figure 5). This continued the sequential conversion of MTBGE to DTBGE as the reaction time progressed till 15h and thereafter, the product distribution remained more or less constant.

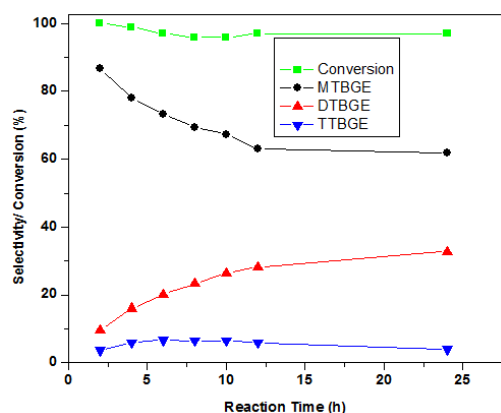


Figure 5: Effect of reaction time. Reaction conditions: glycerol: t-butanol (1:20), 110 °C, time (2-24h), catalyst loading (27.17 wt. %).

Influence of reaction temperature

Influence of temperature on glycerol conversion and product selectivity was investigated over the range of 60 °C-150 °C with a t-butanol/glycerol molar ratio of 20 and a catalyst loading of 27.17 wt%. As expected, the etherification was much slower at the lowest temperature of 60 °C giving the moderate glycerol conversion (34%). Glycerol conversion and selectivity of products was increased with increase in temperature before equilibrium approaching. The highest glycerol conversion is achieved at the lowest reaction temperature, indicating the exothermic property of etherification reaction. Increasing the

reaction temperature from 60 to 150°C resulted in a significant increase in selectivity of TTBG from 0 to 7 % and selectivity of DTBGE from 0 to 22%. Maximum selectivity to DTBGE was found up to 22% at 150 °C in 6 h (Figure 6).

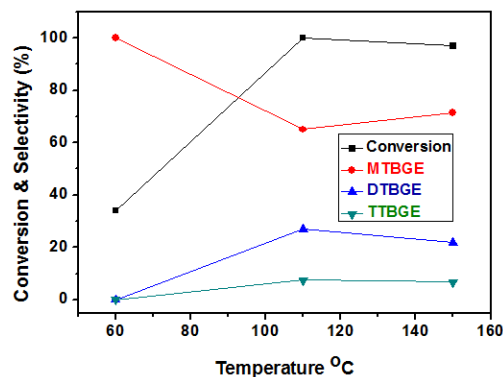


Figure 6: Effect of reaction temperature. Reaction conditions: glycerol: t-butanol (1:20), temperature (60-150 °C), catalyst loading (27.17 wt. %), 6h.

Effect of substrate ratio

In order to achieve higher selectivity's to more substituted ethers like DTBGE and TTBGE effect of excess of TBA was studied by varying the molar ratio of Glycerol: TBA in the range of 1:6 to 1:20. It was observed that the use of excess TBA promoted the formation of both DTBGE and TTBGE. Particularly, the enhancement in selectivity to DTBGE was almost two fold from 13% to 27 %, when the glycerol to TBA ratio was 1:20 (Figure 7).

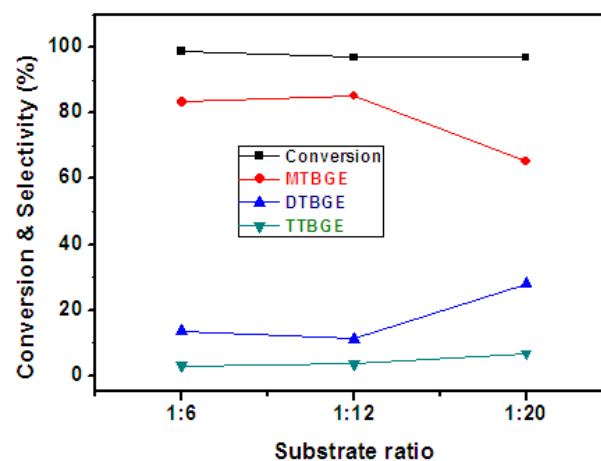


Figure 7: Effect of substrate ratio. Reaction conditions: glycerol: t-butanol (x: y), 110 °C, catalyst loading (27.17 wt. %), 6h.

Effect of catalyst loading

Effect of Mont KSF/O loading was studied at 110 °C with glycerol/TBA ratio of 1:20 (Figure 8). Under optimized reaction conditions catalyst weight in the reaction mixture was varied in from 100mg to 350 mg. The selectivity of DTBGE attained its maximum level of 30% over Mont-KSF/O with 250mg loading.

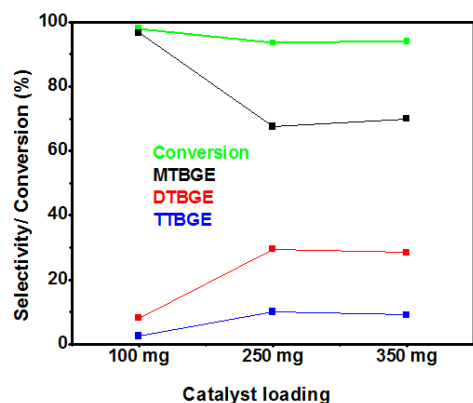


Figure 8: Effect of catalyst loading on conversion of glycerol and selectivity to ethers. Reaction conditions: glycerol: t-butanol (1:20), 110 °C, Mont KSF/O, 6h.

Recycle of the Catalyst

After end of reaction Mont KSF/O catalyst was filtered and washed with methanol and dried at 100 °C for 2h and reused for the subsequent run. Catalyst can be recycled several times without any loss of activity (Figure 9).

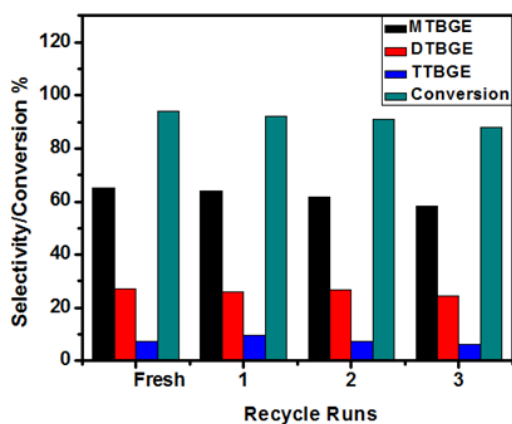


Figure 9: Recycle study of Mont-KSF/O. Reaction conditions: glycerol: t-butanol (1:20), 110 °C, Mont KSF/O, 6h.

Conclusion

Etherification of glycerol with t-butanol was effectively achieved in the presence various commercially available Mont-clay catalysts. Among the different screened catalysts, Mont-KSF/O actively catalyzed the etherification reaction due to its highest acidity as measured by ammonia-TPD (Mont-KSF/O > Mont-K-10 > Mont-Al). In spite of its lower surface area (Mont-KSF/O < Mont-K-10 < Mont-Al) it is active for production of DTBGE and TTBGE. The process was optimized by studying the effect of temperature, molar ratio (glycerol/TBA), catalyst loading and reaction time. It was found that the increase in temperature significantly affected the glycerol conversion and DTBGE formation. Almost complete glycerol conversion was achieved in 6h, at 110 °C with 1:20 molar ratio of glycerol to TBA over 27.17 wt% catalyst loading. Prolonged reaction time

of 24h led to maximum selectivity of ~ 33% to DTBGE. The catalyst could be recycled efficiently with a consistent activity and selectivity.

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