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Green Synthesis of Glycerol Carbonate via Transesterification of Glycerol using Mechanochemically prepared Sodium Aluminate Catalysts

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Abstract

Glycerol, an important by-product from biodiesel production, has significant potential as platform chemical with several different pathways of value addition being investigated. Herein, we report the synthesis of glycerol carbonate via the transesterification of glycerol with dimethyl carbonate using supported sodium aluminate catalysts. The effects of catalyst preparation method, and different metal oxide supports were investigated. Mechanochemically prepared catalysts were more stable than the corresponding catalysts prepared using a wet impregnation technique. Alumina as a support was found to provide the highest level of stability, amongst the metal oxide supports tested. The mechanochemically prepared catalyst with a sodium aluminate loading of 20 wt% supported on alumina, was found to be the most effective catalyst achieving 96 % yield of glycerol carbonate after 60 minutes. The catalysts were thoroughly characterized to investigate the effect of the catalyst synthesis method on the catalyst structure, catalytic activity and stability. Mechanochemically prepared 20 wt% sodium aluminate supported on alumina showed facile recovery and good reusability over four times with only a marginal decrease in activity.
More than a hundred countries are pursuing to achieve a target of net zero emissions by 2050. As a result of the sustainable development scenario, especially in the global transportation sector, increasing attention has turned towards decreasing the reliance on crude oil feedstocks, by blending carbon-neutral biofuels into the fuel mix, e.g. biodiesel. In a typical bio-refinery process, biodiesel is produced from vegetable oils, yellow grease, used cooking oils, or animal fats by transesterification with methanol to give fatty acid methyl esters (FAME) \(^1\). During FAME production, large quantities of waste glycerol are formed as a by-product, which account for 10 wt % of biodiesel produced. As of 2017, global production of biodiesel was 36.1 billion liters annually (IEA, 2019). Europe is the largest producer of biodiesel accounting for 44 % of production, with the Americas (namely USA and Brazil) accounting for 37 % (IEA, 2019). Global prices of glycerol have dropped as a direct result of the increase in biodiesel production. Before the growth in biodiesel production, glycerol was priced at $1.5/kg. Current prices of pure glycerol are US$ 0.27-0.41 per pound with 80 % crude glycerol costing US$ 0.04-0.09 per pound \(^2\). Typically, glycerol from biodiesel production is quite crude, often containing residual base catalyst, methanol, ash and water \(^3\). Due to glycerol’s reactive nature and low cost, there is a great opportunity to transform an abundant glycerol feedstock into a range of value-added chemicals and fuel-additives, thereby promoting an environment friendly circular economic approach to decrease greenhouse gas emissions with the help of sustainable fuel-additives and green renewable solvents.

A variety of catalytic pathways for value-addition to glycerol are possible, which include reforming to produce synthesis gas, photocatalytic reforming for $\text{H}_2$ production \(^4\), esterification to yield glycerol esters \(^5\), dehydration to acrolein, oxidation to dihydroxyacetone, and hydrogenolysis to isomers of propanediol \(^6\). Amongst glycerol valorisation pathways, the carbonation of glycerol to glycerol carbonate (GC) is amongst the most relevant to the bio-refinery processes. Glycerol carbonate can further react to glycidol (GD), hence it requires a delicate balance of number and type of catalyst active sites to tune the product selectivity to glycerol carbonate and avoid the subsequent conversion to glycidol. Glycerol carbonate has numerous
applications, owing to its unique properties of low volatility, biodegradability, and low toxicity as a polar solvent, in healthcare, and as a monomer in synthesis of various renewable polyesters, polycarbonates, and polyurethanes. Glycerol carbonate can also be used in the manufacturing of materials such as coatings, adhesives, foams, lubricants and plasticizers.\textsuperscript{7,8,9}

![Reaction Scheme for synthesis of Glycerol Carbonate from Glycerol and Dimethyl Carbonate](image)

**Figure 1** - Reaction Scheme for synthesis of Glycerol Carbonate from Glycerol and Dimethyl Carbonate

In the current state-of-the-art, several pathways for the production of glycerol carbonate have been explored including, carbonylation with phosgene or carbon monoxide, direct carbonation with CO\textsubscript{2}, and glycerolysis with urea\textsuperscript{10}. However, each carbon source has its own advantages and disadvantages. While, the use CO\textsubscript{2} is essential to mitigate the environmental CO\textsubscript{2} levels by direct carbon capture and utilization, the current bench mark requires the use of sacrificial dehydrating agents such as 2-cyanopyridine or acetonitrile in stoichiometric excess to achieve decent conversions, further adding to the cost of the process, formation of waste byproducts. The use of urea is attractive, as the cost of urea could be slightly lower than cost of dimethyl carbonate, but results in formation of NH\textsubscript{3} as by product, which requires specialized equipment for capture, compression and recycle of NH\textsubscript{3}, in particular in biorefinery processes the scope of using NH\textsubscript{3} has versatile avenues. The use of dimethyl carbonate forms methanol as the byproduct, which is easy to recover and recycle in the biorefinery, especially in the integrated process for production of biodiesel,
FAME via esterification of triglycerides. Hence, the transesterification of glycerol with alkyl carbonates, for instance dimethyl carbonate, is an appealing process, due to the use of moderate reaction conditions, and relatively better conversion and higher GC yield. Synthesis of glycerol carbonate with dimethyl carbonate (DMC) is attractive, as DMC can be produced from CO₂ meaning it is renewable, and it is also non-toxic. The reaction scheme for the production of glycerol carbonate through glycerol and dimethyl carbonate is shown in Figure 1.

Both homogeneous and heterogeneous catalysts have been reported for the reaction. Naik et al. reported the use of the organocatalyst 1-n-butyl-3-methylimidazolium-2-carboxylate (BMIM-2-CO₂). BMIM-2-CO₂ was found to be quite active giving complete conversion of glycerol after 80 minutes using only 1 mol% of catalyst. Ishak et al. reported the use of various ionic liquid catalysts for the reaction. They found Emim[Ac] to be the most active giving 94 % conversion of glycerol with high selectivity to glycerol carbonate of 89 % after 2 hours (Reaction conditions: 120 °C, 1:2 mole ratio (Glycerol:DEC), 0.5 mol% catalyst). Basic ionic liquids have also been reported by Chiappe et al. using N-methyl-N-butylmorpholinium dicyanamide ([Mor₁₂][N(CN)₂]) . However, this catalyst needed a high catalyst loading and long reaction time to achieve high conversion. Tetrabutylammonium salts have also been reported and are effective catalysts for the reaction. Use of alkali-hydroxide homogeneous catalysts such as KOH and NaOH yield complete conversion and high selectivity after 90 minutes. Overall, a multiple number of downstream processes and auxiliary equipment are often required for either recovery and recycle of these homogeneous catalysts or an efficient effluent treatment for mineralization of alkali hydroxides, which limits their industrial application. The majority of heterogeneous catalysts used for the reaction have been based upon basic metal oxides such as magnesium oxide, calcium oxide and barium oxide. Ochoa-Gómez et al. reported the use of CaO and MgO, with CaO proving more active than MgO giving a 91.1 % yield of glycerol carbonate after 90 minutes when calcined at 900 °C (Reaction conditions: 75 °C, 1:5 mole ratio (Glycerol:DMC), 0.1:1 mole ratio (catalyst:Glycerol)). The activity of CaO can be further improved by the impregnation of active species such as chloride salts. Mixed metal oxide catalysts have been widely
reported including Sr-Al, Mg-Ce, Mg$_{1+x}$Ca$_x$O$_2$, Mg-Al-Zr, Mg-Zr-Sr, ZnO-La$_2$O$_3$ and Barium mixed metal oxides. Layered double hydroxides have also been widely reported for the reaction. Catalysts for the reaction can also be prepared from a variety of waste sources such as oil palm ash, steel slag and red mud.

Sodium Aluminate (NaAlO$_2$) is a strong solid base which has gained interest recently as a catalyst for biomass conversion, as it is commercially available and relatively inexpensive. Ramesh et al. investigated the use of spray dried sodium aluminate microspheres. It was found that the spray-dried NaAlO$_2$ had much faster kinetics when compared to the commercial catalyst, yielding 83% glycerol carbonate (Reaction conditions: 3wt% catalyst, 1:2 mole ratio (glycerol:DMC), 30 °C, 30 minutes). Spray drying using glycerol as a template was investigated by Rittiron et al. who also found higher activity when compared to the commercial catalyst. Whilst NaAlO$_2$ is highly active in its pure form, it is also highly hygroscopic and corrosive. For this reason, it is desirable to support NaAlO$_2$ to increase ease of handling. NaAlO$_2$ supported on hydrotalcites have proven to be highly active in the reaction with 10 wt% NaAlO$_2$ on hydrotalcite yielding 93% glycerol carbonate (Reaction conditions: 3 wt% catalyst, 1:2 mole ratio (Glycerol:DMC), 90 °C, 30 minutes).

In this study, the use of sodium aluminate supported on alumina catalysts prepared by mechanochemical synthesis are reported as efficient and reusable catalysts for the production of glycerol carbonate. Preparation of catalysts using mechanochemistry can be environmentally friendly requiring no solvent, and is an overall more simplistic preparation method. The ball milling preparation method was compared with a conventional wet impregnation method. Initially the effect of metal oxide support on activity and stability was investigated, and then the effect of sodium aluminate loading was explored. The process parameters were then optimized to maximize the conversion of glycerol to glycerol carbonate.
2. Experimental Section

2.1 Materials and Methods
All chemicals were of AR grade unless otherwise stated and used without any further purification. Glycerol, dimethyl carbonate, methanol, sodium aluminate (tech.) and silicon dioxide were purchased from Alfa Aesar. Aluminium oxide and magnesium oxide were purchased from STREM chemicals. P90 Titanium dioxide was purchased from Evonik industries. All catalysts were prepared in house.

2.2 Catalyst Synthesis
A series of supported sodium aluminate catalysts were prepared by mechanochemical methods. The required amount of sodium aluminate (20 wt% of catalyst) and metal oxide support (80 wt% of catalyst) were well mixed and loaded into a 125 mL agate grinding jar with two 20 mm diameter agate grinding balls. Milling was typically performed at 450 RPM for 1 hr using a Retsch PM100 Planetary Ball Mill, as shown in Figure 2.

![Figure 2 - Catalyst Synthesis using a Planetary Ball Mill](image)

A 20 wt% sodium aluminate on alumina catalyst was also prepared using a simple wet impregnation method. Here 0.4 g of sodium aluminate was dissolved in 20 mL of distilled water. To this
1.6 g of alumina support was added under stirring, and stirred for 1 hr. Subsequently excess water was
removed, and the catalyst was dried at 120 °C overnight.

2.3 Catalyst Characterization

The prepared catalysts were characterized by X-ray diffraction, elemental analysis, FT-IR, TGA, surface
basicity measurements, CO₂-TPD, SEM and EDX. X-Ray scattering measurements were made
with Panalytical X-Pert Pro MPD diffractometer with Ni filtered CuKα radiation (1.5405 Å). The
diffractograms were recorded with step size of 0.016° from 5 ° to 80 °. Fourier-transform infrared (FT-IR)
spectra of neat catalyst samples were recorded using an Agilent Cary 630 FTIR spectrometer.

Thermogravimetric analysis (TGA) were recorded using a Q5000 thermogravimetric analyzer (TA
Instrument Company) with a ramp mode of 10 °C/min to 600 °C, a nitrogen flow of 25 mL/min using
platinum pans. Basicity of the prepared catalysts was determined by an acid-base titration method and CO₂
Temperature Programmed Desorption (TPD). For acid-base titration the solid catalysts were stirred in 25
mL of 0.1 M HCl solution for 6 hours, and then titrated with 0.1 M NaOH solution to calculate the
basicity. CO₂-TPD measurements were recorded using a Micromeritics MicroActive AutoChem II 2920
using 0.1 g of catalyst powder. The catalyst samples were heated under helium flow to 500 °C at a rate of
10 °C/min for 60 minutes. The sample was cooled to 50 °C, then 2 % CO2 in helium was passed over the
sample for 4 hours. After this the sample was heated from 50 °C to 900 °C at 10 °C/min under flow of
helium. All gas flow rates were 30 mL/min. Scanning Electron Microscopy (SEM) images were recorded
using an FEI Quanta FEG Environmental SEM.

2.4 Reaction Procedure

The reaction was carried out in a 100 mL two-necked round bottom flask, equipped with magnetic stirring
and a condenser. The flask was kept in an isothermal oil bath at a known temperature and mechanically
agitated at the required speed. In a typical reaction, glycerol (5 g, 0.054 mol), dimethyl carbonate (14.59 g,
0.162 mol), and catalyst (10 wt% with respect to glycerol) were loaded into the round-bottom flask and
stirred at 800 RPM for 1 hour. Reaction samples were withdrawn periodically for analysis. The analysis of
the reaction was carried out using an Agilent 7820A GC equipped with a HP-5 capillary column (30 m x
0.32 mm x 0.25 µm) and a flame ionization detector. The inlet is set at 250 °C and the FID is set to 300 °C.
A split ratio of 80:1 is used with a split flow of 80 mL/min. The oven temperature is as follows; 120 °C
ramping to 260 °C at a rate of 15 °C/min.

For reusability studies, the catalysts were separated from the reaction mass by centrifugation and
then dried overnight in an oven at 120 °C.
3. Results and Discussion

3.1 Effect of Wet Impregnation vs. Mechanochemical Preparation

In Figure 3, 20 wt% sodium aluminate supported on alumina prepared by conventional wet impregnation is compared against the same catalyst prepared using a planetary ball mill, and a physical mixture of sodium aluminate and alumina.

![Figure 3 - Effect of Catalyst Preparation Method for 20 wt% sodium aluminate/Al₂O₃ catalyst.](image)

Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 10 wt% catalyst loading, 90 °C, 30 min.

It can be seen in Figure 3 that the initial activity of the catalyst prepared by a wet impregnation method has a higher initial activity than that of the catalyst prepared by ball mill. However, the stability of the wet impregnation catalyst is quite poor exhibiting a large reduction in glycerol conversion of 27 % upon the first reuse of the catalyst. Conversely the catalyst prepared via ball mill shows a much higher stability when comparing fresh and reused activity levels, with a smaller 3.3 % loss in conversion upon reuse.
The FTIR spectra of fresh and reused catalysts prepared by both ball mill and wet impregnation methods (20 wt% loading of sodium aluminate) are shown in Figure 4. Neat alumina exhibits a broad peak at 3435 cm\(^{-1}\) due to the presence of hydroxyl groups on the surface of the solid. The ball mill catalyst exhibits spectra highly similar to that of the neat alumina. The peak at 1394 cm\(^{-1}\) can be associated with the presence of carbonates on the surface of the catalyst \(^3\). Other characteristic peaks associated with NaAlO\(_2\) loading such as O-O, Al-O, and O-Na-O are not visible on the FT-IR spectra.

![FTIR Spectra of Fresh and Used 20 wt% sodium aluminate/Al\(_2\)O\(_3\) catalyst](image)

**Figure 4** - FTIR Spectra of Fresh and Used 20 wt% sodium aluminate/Al\(_2\)O\(_3\) catalyst

The structure of catalysts prepared by wet impregnation is different from that of the ball mill preparation, with the spectra indicating the possible formation of aluminium hydroxide resulting from the hydrolysis of sodium aluminate. Peaks in the range of 3300 to 3700 cm\(^{-1}\) can be assigned to the stretching vibration of the hydroxyl groups in Al(OH)\(_3\), whilst the peak observed at 1021 cm\(^{-1}\) is as a result of the Al-O bonds present. The FT-IR spectra of both the ball mill and wet impregnation catalysts remains unchanged upon reuse. However, both catalysts exhibit signs of adsorbed glycerol from the reaction. The peak at 997 cm\(^{-1}\)
can be assigned to the vibration of the skeleton C-C of glycerol, with peaks at 1031 and 1113 cm$^{-1}$ as a result of C-O bond stretching. Peaks due to the C-H bond stretching of glycerol are observed at 2874 and 2932 cm$^{-1}$.

The XRD structure of the fresh and used catalysts prepared by ball mill and wet impregnation methods are shown in Figure 5 (the inset picture shows the XRD data for pristine sodium aluminate and alumina support). The structure of the pristine alumina support shows peaks at 37.4°, 42.9° and 67.3° corresponding to (311), (400) and (440) reflections of γ-Al$_2$O$_3$. The XRD for the commercial sodium aluminate shows two crystalline phases attributable to sodium aluminate (20.6°, 21.3°, 30.3°, 33.3°, 34.3°, 35.0°, 42.2°, 48.3°, 51.9°, 57.6°, 61.9°, 63.7° and 68.8°) and sodium carbonate (33.3°, 37.5° and 46.4°)$^{35}$.

![Figure 5 - XRD patterns of Fresh and Used 20 wt% sodium aluminate/Al$_2$O$_3$ catalysts](image)
The XRD patterns for the ball mill catalysts shows integration of the crystalline structure of sodium aluminate onto the surface of the alumina support. The pattern of the used ball mill catalyst also shows the same characteristic peaks as the fresh catalyst, indicating no major structural changes in the catalyst after use. Conversely the pattern for the catalyst prepared by wet impregnation shows crystalline peaks at 18.7°, 20.4°, 27.9°, 40.7° and 53.3° which can be attributed to the formation of aluminium hydroxide. The used wet impregnation catalyst retains most of the characteristic peaks associated with the aluminium hydroxide.

The poor stability of the wet impregnation catalyst can be attributed to the formation of sodium hydroxide and aluminium hydroxide, via the hydrolysis of sodium aluminate during catalyst preparation. The sodium hydroxide leaches from the surface of the alumina support and contributes to the conversion in a homogeneous manner. The catalyst prepared by ball mill also showed higher initial activity and greater catalyst stability when compared against a physical mixture of sodium aluminate and alumina. This indicates that the ball mill synthesis provides a greater level of dispersion of sodium aluminate on alumina. The physical mixture shows a greater loss in activity of 5.5 % conversion, which may be due to higher levels of sodium aluminate because of weaker levels of interaction.

The SEM images shown in Figure 6 – SEM and EDX images of (a,c) 20 wt% SA/Al2O3 (B.M.) and (b,d) 20 wt% SA/Al2O3 (W.I.) show that both the sodium aluminate on alumina catalysts prepared by ball mill and wet impregnation show a spherical morphology. EDX mapping of the two catalysts also show that a good dispersion of sodium on the support surface is achieved through both preparation methods.
Figure 6 – SEM and EDX images of (a,c) 20 wt% SA/Al₂O₃ (B.M.) and (b,d) 20 wt% SA/Al₂O₃ (W.I.)
3.2 Screening of Initial Catalyst Activity and Stability

The prepared catalysts were screened in the reaction of glycerol with dimethyl carbonate to yield glycerol carbonate. NMR spectroscopy confirmed that no glycidol was produced during the reaction, meaning all catalysts gave 100 % selectivity to glycerol carbonate. For reference a blank reaction with no catalyst was performed, and no glycerol conversion was observed after 60 minutes. The activity and stability of fresh and reused catalysts prepared by mechanochemical methods are shown below in Figure 7.

Figure 7 - Catalytic Activity of Fresh and Used 20 wt% sodium aluminate catalysts supported on different metal oxides. All catalysts were prepared by Ball Milling. Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 10 wt% catalyst loading, 90 °C, 30 min.
From Figure 7 it can be noted that sodium aluminate supported on MgO is the most active catalyst for the reaction, this corresponds well with the high basicity of 26.3 mmol g$^{-1}$ observed. Activity follows the following trend; MgO > TiO$_2$ > Al$_2$O$_3$ > SiO$_2$. This correlates well with the CO$_2$-TPD profiles of the prepared catalysts with MgO the only catalyst exhibiting weak, moderate, and strong basic sites. All other prepared catalysts showed only weak and moderate sites, as shown in Figure 8. Strength and number of basic sites appears to be a key factor in the activity of the catalyst. There appears to be no correlation between the surface area of the catalysts, shown in Table 1, and the activity of the catalysts. Whilst activity of a catalyst is an important consideration, stability and reusability of the catalyst is also desirable. When considering stability, sodium aluminate supported on Al$_2$O$_3$ is the most stable catalyst with only a marginal decrease in activity upon reuse. All other catalysts show significant loss in activity upon reuse indicating leaching of the active sodium aluminate phase from the support. It is indicative of greater interaction between sodium aluminate and the alumina support leading to greater catalyst stability. The catalyst
stability is as follows; \( \text{Al}_2\text{O}_3 > \text{MgO} > \text{SiO}_2 > \text{TiO}_2 \). Due to the increased stability, alumina was chosen as the support for further study.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Basic sites (mmol g(^{-1}))</th>
<th>Surface Area (m(^2)/g(^{a}))</th>
<th>Pore Volume (cm(^3)/g(^{b}))</th>
<th>Pore Size (Å(^{c}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% SA/Al(_2)O(_3) (WI)</td>
<td>1.8</td>
<td>183.28</td>
<td>0.168</td>
<td>36.56</td>
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<tr>
<td>20 wt% SA/Al(_2)O(_3)</td>
<td>2.2</td>
<td>178.25</td>
<td>0.166</td>
<td>37.24</td>
</tr>
<tr>
<td>20 wt% SA/TiO(_2)</td>
<td>2.2</td>
<td>40.52</td>
<td>0.132</td>
<td>130.52</td>
</tr>
<tr>
<td>20 wt% SA/SiO(_2)</td>
<td>2.2</td>
<td>87.90</td>
<td>0.394</td>
<td>179.43</td>
</tr>
<tr>
<td>20 wt% SA/MgO</td>
<td>26.3</td>
<td>38.01</td>
<td>0.177</td>
<td>186.28</td>
</tr>
</tbody>
</table>

\(^{a}\text{BET Surface Area}\)

\(^{b}\text{Single point adsorption}\)

\(^{c}\text{Adsorption Average Pore Width}\)
3.4 Effect of Sodium Aluminate Loading on Alumina

The effect of increasing the sodium aluminate loading on glycerol conversion is shown in Figure 9. It can be noted from Figure 9 that pure sodium aluminate exhibits similar glycerol conversion when compared to 20 wt% SA/Al$_2$O$_3$, 98 % and 96 % conversion respectively after 60 minutes. Whilst activity of the catalysts is similar, supported sodium aluminate has the advantage of being easier to handle, as pure sodium aluminate is corrosive and hygroscopic. Whilst fresh alumina provides a small amount of activity, the majority of the activity of the catalysts is as a direct result of the supporting of sodium aluminate.

**Figure 9** - Effect of Sodium Aluminate Loading on Glycerol Conversion. *Reaction conditions: glycerol (0.054 mol), DMC (0.162 mol), 10 wt% catalyst loading, temperature 90 °C, reaction time 60 min. Pure SA loading (0.1 g).*

Increasing the loading of sodium aluminate results in an increase in the activity of the catalyst up until 20 wt% loading, after which a further increase in the sodium aluminate loading provides no further increase in
the rate of glycerol conversion. A 20 wt% loading exhibits 95 % glycerol conversion after 60 minutes, with
a further increase of 10 wt% in loading resulting in a decrease to 92 % glycerol conversion in the same time.

3.5 Catalyst Reusability

Several reaction cycles were performed to evaluate the stability and reusability of the catalysts. It is
important from an environmental and economical point of view that catalysts retain high levels of activity.
The catalysts were separated from the reaction mixture by centrifugation, and dried overnight at 110 °C.
The results are shown in Figure 10.

Figure 10 - Reusability of 20 wt% sodium aluminate/Al₂O₃ catalyst. Reaction conditions: glycerol (0.054
mol), DMC (0.162 mol), 10 wt% catalyst loading, 90 °C, 60 min.
A gradual loss in the activity of the catalyst was observed for the catalyst from 1st to 4th reuse. Glycerol conversion decreased from 96.7% to 83.3% after 4 reaction cycles. While the recycling tests are performed at relatively high conversion, preventing a true quantitative estimation of the deactivation of initial activity, a clear trend indicating relatively higher stability of NaAlO₂/Al₂O₃ catalyst can be detected. It can be seen in Figure 5 that the XRD of the used catalyst remains relatively unchanged when compared to the fresh catalyst. The presence of adsorbed reactants on the used catalyst is observed with FT-IR shown in Figure 4. Adsorbed reactants are also observed in the TGA of the used catalyst as shown in Figure 11. The fresh catalyst loses roughly 12.5% weight when heated to excess of 400 °C. The used catalyst loses around 25% wt loss when heated to the same temperature, indicating presence of adsorbed species. ICP analysis of the reaction mixture after use showed the presence of very small amounts of sodium and aluminum, which may indicate that catalyst deactivation is a result of combined effect of the loss of catalyst particles due to attrition, and a very small amount of sodium aluminate leaching from the surface of alumina, and adsorption of organics during the reaction. Further, hot filtration test was performed to confirm the presence of leached sodium aluminate species in solution. The reaction was observed to progress further, albeit slowly, after removal of the solid catalyst.
4. Conclusions

Alumina supported sodium aluminate catalysts were successfully employed for the green synthesis of glycerol carbonate from glycerol and dimethyl carbonate under ambient conditions. Catalysts prepared using mechanochemical preparation were more stable than those prepared by a wet impregnation method. Preparation using wet impregnation resulted in the formation of aluminum hydroxide and sodium hydroxide via the hydrolysis of sodium aluminate. Alumina was found to provide the highest level of sodium aluminate stability out of the metal oxides tested. A loading of 20 wt% sodium aluminate on alumina was found to be the most active catalyst with 96 % glycerol conversion after 1 hour. The catalyst showed relatively good reusability, with a small decrease in glycerol conversion of 3.4 % upon reuse.

Figure 11 – TGA of Fresh and Used 20 wt% Sodium Aluminate/Al₂O₃ catalysts prepared by Ball Mill
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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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