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Direct carbonation of glycerol with CO_2 catalyzed by metal oxides

Leonardo P. Ozorio,[a] Claudio J. A. Mota*[a],[b],[c]

Abstract: Five metal oxides (ZnO, SnO_2, Fe_2O_3, CeO_2, La_2O_3) were produced by the sol-gel method and tested in the direct carbonation of glycerol with CO_2. Initial tests with Fe_2O_3 showed that the best reaction condition was 180 °C, 150 bar and 12 h. The other oxides were evaluated at these conditions and were all active to the formation of glycerol carbonate. Zinc oxide was the most active catalyst, with a yield of 8.1% in the organic carbonate. The catalytic activity decreased upon washing and drying the ZnO catalyst between the runs. Nevertheless, the activity is maintained if the ZnO is washed and calcined at 450 ºC between the runs. FTIR and TGA results indicated the formation of $ZnCO_3$ as the main cause of catalyst deactivation, which may be decomposed upon calcination of the material. No appreciable leaching of Zn was observed, indicating a truly heterogeneous catalysis.

Introduction

Carbon dioxide is a major greenhouse gas. Its concentration in the atmosphere has reached alarming levels in recent decades, leading to climate changes due to the elevation of the temperature of the planet.[1] In the last United Nations Conference on Climate Changes (COP-15), countries have agreed to reduce their CO_2 emissions to keep the increase of temperature within 1.5 ºC until the end of the century. Therefore, the studies on environmental issues and carbon dioxide mitigation are increasing in importance.[2-4]

Much of the CO_2 released into the atmosphere is due to the burning of fossil fuels, which are currently the main source of energy. One of the options for reducing the level of this gas in the atmosphere is its capture and conversion in products of industrial interest and high added-value.[5]

Carbon dioxide has been used as coolant fluid in conditioned air systems, in fire extinguishers, in food preservation and beverage manufacturing. However, its use as raw material in the chemical industry is still limited to few processes, especially the manufacture of urea and salicylic acid.[6,7] CO_2 has a high thermodynamic stability and low chemical reactivity; thus, any industrial process of carbon dioxide chemical transformation may be energy intensive and requires the use of catalysts. Products such as hydrocarbons, methanol and organic carbonates are among those of potential interest to be synthesized using carbon dioxide as feedstock.[6-8]

Cyclic carbonates with five-membered rings are used as aprotic polar solvents, precursors for the synthesis of polycarbonates and polyurethanes, electrolytes in lithium batteries, production of drugs, among others.[9-11] Synthesis of cyclic carbonates can be accomplished by coupling carbon dioxide with epoxides, polyalcohols and oxidative carboxylation of olefins. [9,12-15]

The process of obtaining cyclic carbonates via the direct reaction between glycols and CO_2 is more sustainable and ecological than the reaction with epoxides or use of phosgene ($COCl_2$).[16-18] However, this route has thermodynamic limitations and the yields are usually low if water suppressor agents are not used to shift equilibrium.[19]

We have shown that NaY zeolite impregnated with Ag, Zn and Sn oxides are good catalysts for the direct carbonation of glycerol to glycerol carbonate.[20] The parent NaY zeolite showed no conversion at 180 °C, 3 hours and 100 Bar, but when impregnated with the metal oxides the yield of glycerol carbonate was up to 5.8%, near the thermodynamic equilibrium at the reaction conditions.

Due to the adsorption of CO_2 on the surface of metallic oxides, it is possible to use these materials as catalysts in the conversion of the gas.[20-26]

La_2O_3 impregnated with different Cu contents were evaluated in the reaction between glycerol and CO_2 in the presence of CH_3CN as dehydrating agent. The catalyst with 2.3% of Cu over La_2O_3 showed glycerol conversion of 33.4% and 45.4% selectivity to glycerol carbonate. Monoacetin was also observed with a selectivity of 52.9%, at 150 °C, 12 hours and 70 Bar. Authors stated that the size of the Cu particles and the Cu/ La_2O_3 basic sites have a significant effect on the conversion to glycerol carbonate.[24]

Liu et al. synthesized CeO_2 with different morphologies using three methods: traditional precipitation, hydrothermal synthesis and sol-gel citrate. These materials were tested in the synthesis of glycerol carbonate. Authors observed that CeO_2 exhibits high activity at 150 °C, 40 Bar and 5 hours. The influence of different dehydrating agents and solvents was also evaluated. 2-Cyanopyridine and DMF were used as dehydrating agent and solvent, respectively, yielding 78.9% of glycerol carbonate. The catalyst could be reused in five consecutive runs upon regeneration at 400 °C for 5 h.[26]

Zhou et al. studied[27] the use of terminal propargylic alcohols, in reactions between vicinal alcohols and CO_2 in the presence of silver catalysts. The authors stated that they were able to produce glycerol carbonate in 82% of yield with 3-Hydroxy-3-methylbutan-2-one as by-product in 83% of yield, being both products with high added value compared to glycerol and CO_2.

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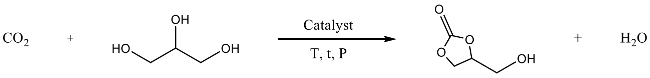
The authors suggested that this reaction pathway may be a viable alternative to overcome the thermodynamic limitations.

The use of dehydrating agents and solvents shifts the equilibrium, increasing the yield of glycerol carbonate. However, they lead to many undesired by-products which make the purification process expensive. Therefore, the search for more sustainable dehydrating agents is necessary.[28]

In this study we have synthesized Zn, Sn, Fe, Ce and La oxides by the sol-gel method to test them as catalysts in the direct carbonation of glycerol with CO_2 (Scheme 1). As the main objective is the study of the catalytic activity of the materials, no dehydrating agent was added. Therefore, the reactions were limited by the thermodynamic equilibrium.

The sol-gel method is successfully used in the production of metal oxide material for uses in ceramics, glass, films and fibers.[29,30] In this work, we used this methodology to prepare different metal oxides through the use of polyvinyl alcohol (PVAl) as template.[31-33]



Scheme 1. Reaction of CO_2 with glycerol to produce glycerol carbonate.

Results and Discussion

The prepared metal oxide catalysts were analyzed by XRD. Figure 1 shows the diffraction patterns, which correspond to the desired oxide by comparison to the Joint Commitee on Powder Diffraction Standards (JCPDS) files contained in the International Center for Diffraction Data (ICDD) database.[34]

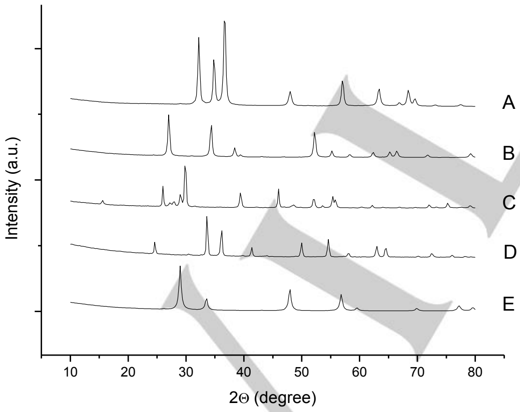


Figure 1. XRD of the prepared metal oxides: (A) ZnO, (B) SnO_2, (C) La_2O_3, (D) Fe_2O_3 and (E) CeO_2.

Initial tests were carried out with Fe_2O_3 to screen the best reaction conditions. Figure 2 shows the effect of the pressure on the yields of glycerol carbonate at 180 °C and 3 h of reaction time. As would be expected, the increase in pressure leads to higher yield of product.

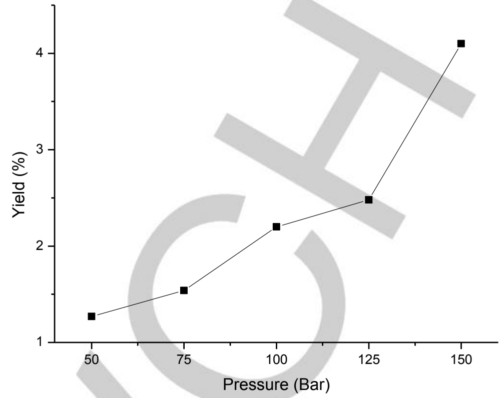


Figure 2. Yield of glycerol carbonate over Fe_2O_3 as a function of the pressure at 180 ºC and 3 h**.**

Figure 3 shows the yield of glycerol carbonate with varying reaction time, at 180 ºC and 150 bar of pressure over Fe_2O_3. It can be seen that after 12 h the yield is almost constant, around 6.8%. This is associated with the equilibrium conditions, which has been calculated to be near this value at non-supercritical conditions.[19]

The remaining catalysts were tested at 180 ºC, 150 bar and 12 h of reaction time. The results are shown in figure 4.

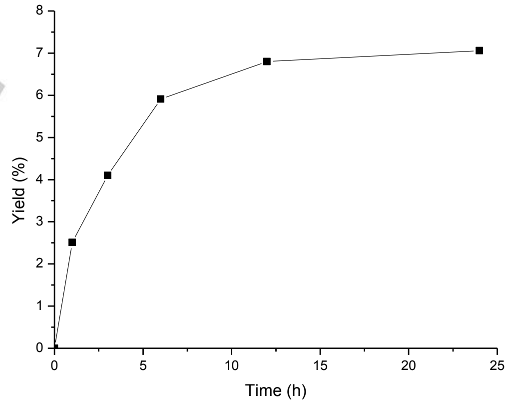


Figure 3. Yield of glycerol carbonate over Fe_2O_3 as a function of time at 180 ºC and 3 h.

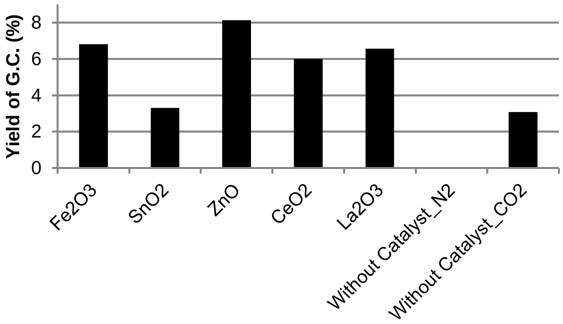


Figure 4. Yield of glycerol carbonate over different metal oxide catalysts at 180 ºC, 150 bar and 12 h.

The reaction without catalyst, just pressurizing the glycerol with CO_2 at the reaction conditions, yielded 3% of glycerol carbonate. A similar yield was observed with SnO_2, indicating that the material has negligible activity at the reaction conditions. The best performance was observed with ZnO, which showed 8.1% yield of glycerol carbonate. La_2O_3 and Fe_2O_3 gave approximately the same yield of glycerol carbonate, near 7%, whereas CeO_2 presented 6% of glycerol carbonate at the reaction conditions. The results clearly shows that all the synthesized oxides are active in the direct carbonation of glycerol. No other organic product was observed at the conditions used. It is worth to mention that the liquid fraction, collected after the reaction using ZnO, was analyzed by ICP to test for leaching. The value of 3.7 μg of zinc per gram of sample is somewhat higher than the value of 0.6 μg of zinc per gram of the pure glycerol used in the experiments. However, it shows that leaching of the catalyst to the liquid phase is not expressive and the catalysis is truly heterogeneous.

To better understand the nature of the active sites and reactivity of the catalysts, we have chosen the ZnO system. A sample of zinc oxide synthesized without the addition of the polyvinyl alcohol was also tested in the reaction and showed 5.3% yield of glycerol carbonate at the same reaction conditions. This value is lower than the yield observed with the same oxide synthesized in the presence of PVAl. The difference in activity may be related with the textural properties of the materials. Whereas the ZnO synthesized without the addition of PVAl showed 0.9 m²/g of surface area, the catalyst prepared in the presence of PVAl showed a significantly higher area of 14 m²/g. The larger surface area can provide more active sites, explaining the higher yield of glycerol carbonate. The presence of the polyvinyl alcohol during the synthesis kept the ZnO crystals more spaced from each other. After calcination, unfilled gaps between the crystals may be formed, leading to a porous material with higher surface area. Figure 5A shows the SEM image of the ZnO prepared with the addition of PVAl. The sponge-like morphology is consistent with the SEM results of other oxide materials synthesized in the presence of PVAl.[35] ZnO prepared without the addition of PVAl in the synthesis medium presents a bulkier morphology, consistent with a more compact aggregation of the crystal (figure 5B).

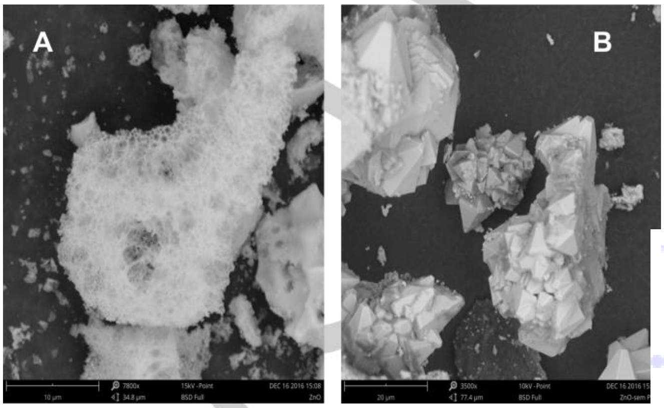


Figure 5. SEM Images: (A) ZnO synthesized with PVAl, (B) ZnO synthesized without PVAl.

The reuse of the ZnO catalysts synthesized in the presence of PVAl was carried out considering two different post-treatments. In the first case, the ZnO was washed with 30 ml of methanol and dried at 160 ºC between the reactions. A gradual loss of activity occurred and after 3 consecutive runs the yield of glycerol carbonate was 4.8 %. The second procedure consisted in washing the material with 30 ml of methanol followed by calcination at 450 ºC. No significant loss of activity was observed after four consecutive runs (Fig. 6). A thermogravimetric analysis (TGA) of the ZnO subjected to washing and drying after the three runs showed 42% of mass loss up to 477 °C, indicating the desorption or decomposition of species on the surface. On the other hand, the TGA analysis of the calcined catalyst after four runs showed no appreciable mass loss in the same temperature range, indicating that calcination has completely regenerated the catalyts (figure 7).

The comparative FTIR analysis between the ZnO before and after pressurization with CO_2 under the reaction conditions is shown in figure 8. One can see the intense bands at 1526 and 1387 cm^{-1}, in addition to bands of lower intensity in the region from 1050 to 700 cm^{-1}, all of which refer to the formation of polydentate carbonate species.[36-40] The FTIR spectrum of ZnO pressurized with CO_2 is similar to the spectrum reported for $ZnCO_3$ nanoparticles,[41] suggesting that some phase of zinc carbonate may be formed upon pressurization with CO_2 at the reaction conditions.

The XPS analysis of the ZnO catalyst before and after reaction did not indicate any major change in the oxidation state of the zinc atom. The spectra (not shown) presented two peak components with binding energy of 1021 eV and 1044 eV, which have being referred to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively, characteristic of Zn-O bond. In the spectrum of the regenerated catalyst (after calcination) it was also noticed that the width of the peak at half height had changed, with the FWHM of Zn $2p_{3/2}$ of 1.932 eV, whereas for the fresh catalyst the value was 1.524 eV. These data may indicated that after calcination there should be some agglomeration leading to slightly larger particle size.[42,43]

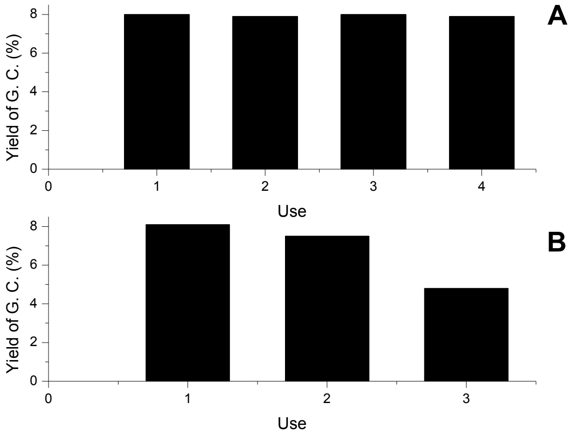


Figure 6. Yield of glycerol carbonate upon the reuse of ZnO: (A) calcination at 450 ºC between the runs; (B) drying at 160 ºC between the runs.

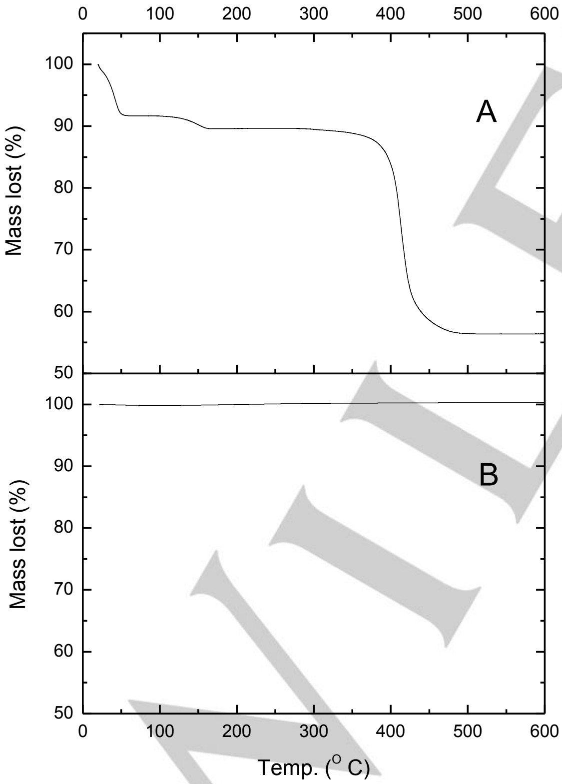


Figure 7. TGA profiles: (A) ZnO upon washing with methanol and drying at 160 ºC; (B) ZnO upon washing with methanol and calcination at 450 ºC.

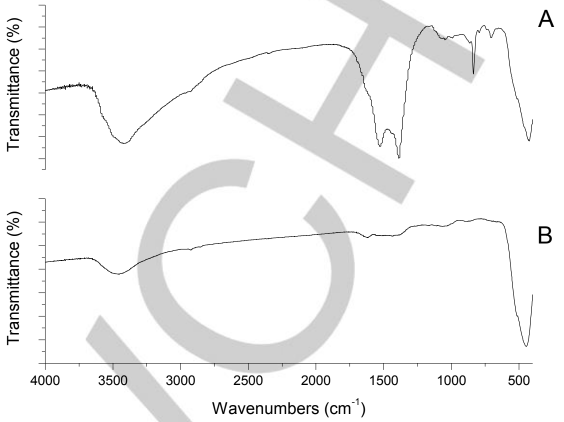


Figure 8. FTIR spectra: (A) ZnO after pressurization with CO_2, (B) ZnO.

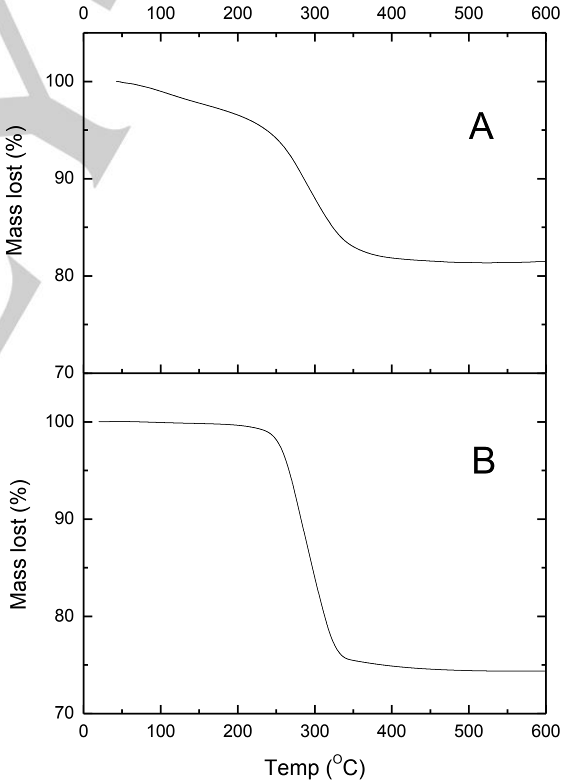


Figure 9. TGA profiles: (A) ZnO after pressurization with CO_2, (B) $ZnCO_3$.

Catalytic test with commercial zinc carbonate was carried out and showed the same yield of glycerol carbonate of the blank reaction, without any catalyst. In addition the reaction of glycerol and $ZnCO_3$ at the same conditions, with N_2 as pressurizing gas, did not yield any glycerol carbonate. Therefore, we should conclude that $ZnCO_3$ is neither a catalyst nor is involved in the mechanistic pathway of the glycerol reaction with CO_2 in the presence of ZnO. In fact, the formation of zinc carbonate phases on the catalyst surface may be the cause of deactivation, when no calcination is performed. Figure 9 shows the TGA profiles of ZnO pressurized with CO_2 and $ZnCO_3$. Both present a similar profile, with the maximum temperature of weight loss aroung 350 ºC. These data support the FTIR results and point out to the formation of $ZnCO_3$ as the most probable cause of catalyst deactivation. Upon calcination, the carbonate is decomposed and the catalytic activity restored, indicative of the regeneration of the catalyst.

The proposed mechanism may involves the reaction of glycerol with the zinc oxide surface to form an adsorbed alkoxide, which then attacks the CO_2 molecule to form a carboxylate intermediate. In the sequence, the secondary hydroxyl of the glycerol may attack the carboxyl group to produce the cyclic carbonate (figure 10).

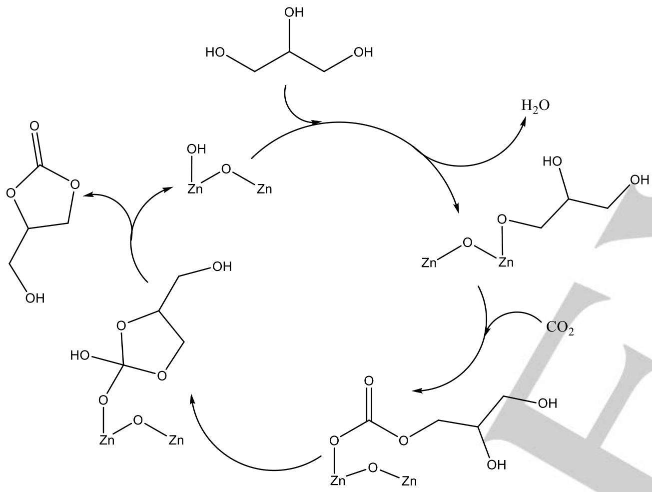


Figure 10. Possible mechanistic scheme for the formation of glycerol carbonate over zinc oxide catalyst.

Conclusions

Five different metal oxides (Fe, Zn, La, Ce and Sn) were prepared by the sol-gel method in the presence of polyvinyl alcohol. All were active to the formation of glycerol carbonate in the reaction of CO_2 with glycerol at 180 ºC and 150 bar. Zinc oxide showed the best performance with a yield of glycerol carbonate of 8.1% after 12 h of reaction time. This value is close to the thermodynamic equilibrium calculated at non-supercritical conditions.

Loss of catalytic activity was observed upon drying the catalyst at 160 ºC between the runs and was associated to the formation of $ZnCO_3$ phase. On the other hand, calcination of the ZnO catalyst at 450 ºC completely recover the catalytic activity, due to the decomposition of the carbonate phase and regeneration of the catalyst.

Experimental Section

Preparation of the catalysts

Two aqueous solutions were prepared: one saturated solution with the metal salts ($SnCl_2$, $Fe(NO_3)_3$, $Zn(NO_3)_2$, $Ce(NO_3)_3$, $La(NO_3)_3$) and other with polyvinyl alcohol (10 wt%). The solutions were mixed, maintaining the metal ion:monomeric unit ratio equal to 1:3, magnetically stirred for 3 hours at 60 ºC and then heated to completely evaporate the water. The resulting material was heated, with the aid of a silicone oil bath, to 250 °C and kept at this temperature for 30 min to decompose the polymer, and obtaining the precursor powder of the catalysts. The metal oxides are obtained after calcination of this precursor powder at 450 °C (1 °C / min) for 4 h, except for the lanthanum oxide precursor which was calcined at 850 °C. This procedure is similar to that described by Fernandes to obtain other metal oxide nanoparticles.[31-33]

The materials were characterized by BET Surface Area, using nitrogen adsorption isotherm, X-ray Diffraction (XRD), thermogravimetric analysis (TGA), Fourier Transform Infrared (FTIR), X ray photoelectron spectroscopy (XPS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Scanning Electron Microscopy (SEM).

Catalytic Test

The catalytic tests were carried out in a 100 ml Parr reactor with 25.2 g glycerol (analytical grade) and the metal oxide (mass referring to 2 mmol of the metal), which was previously dried at 160 °C for 30 min. In all tests the system was initially cooled to 0 ºC, pressurized with 55 bar of CO_2 (99.999%) and heated to 180 °C. Upon heating, the pressure in the system increased and were controlled to the desired value at the desired temperature by releasing the excess of CO_2. At the end, the system was cooled down, pressured was released and the catalysts was vacuum filtered on a glass membrane. About 0.5 g of the liquid fraction was diluted in methanol in a 5 mL volumetric flask. Tetraethyleneglycol (internal standard) was added to the samples, which were then analyzed by gas chromatography coupled to a mass spectrometer (Agilent 5975). The yield of glycerol carbonate was obtained using a calibration curve.

- Reuse test

Two procedures were employed: in the first, the ZnO material was washed with 30 mL of methanol and dried at 160 °C for 30 min between the runs. The second procedure involves washing the material with 30 mL of methanol followed by calcination at 450 °C for 60 min, before using in a subsequent run.

Acknowledgements

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Keywords: Glycerol • CO2 • Cyclic carbonates • Metal oxide • Zinc Oxide

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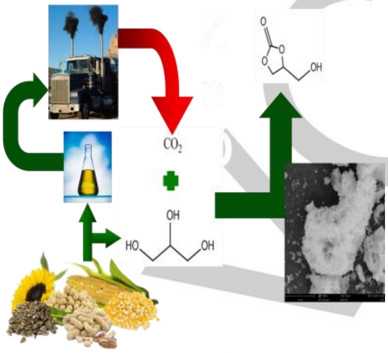

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