Synthesis of Glycerol Carbonate over Hydrotalcite Catalyst

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Glycerol carbonate is a multifunctional compound usable as solvent, additive, monomer, and chemical intermediate. In this work we have studied the possibility of preparing glycerol carbonate in high yields and selectivity. The synthesis is based on glycerine carbonylation with urea in the presence of a heterogeneous Zn-Al-HTC. Zinc-aluminium hydrotalcite like compound (Zn-Al-SO_4) with a molar ratio of 3, containing sulphate anion, was synthesized at room temperature by the co-precipitation method. The catalyst was characterized by X-ray powder diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, inductively coupled plasma atomic emission spectroscopy and elemental analysis. The surface acidity was measured by thermogravimetric analysis of adsorbed n-butylamine. To determinate the optimal parameters, we investigate the influence of the reaction temperature, reaction time, the molar ratio of glycerol to urea and amount of catalyst. Synthesized glycerol carbonate was analyzed by GC–MS/MS.

Keywords: glycerol valorization, glycerol carbonate, hydrotalcites, urea

In todays' context of global warming there is a continuous research effort to find alternative routes to replace fossil fuels with environmentally friendly, renewable bio-derived fuels. One of the most commonly used alternative fuels is the biodiesel, obtained at industrial scale by transesterification of vegetable fats with methanol, process in which glycerine results as a by-product [1]. Recently, fuel distribution stations, sells only blends of diesel fuel and biodiesel. Because biodiesel price is higher than of diesel fuel price, the researchers searched for solutions for minimizing it. One way to reduce the price of biodiesel, is the recovery and purification of crude glycerine obtained as by-product [2].

An important direction for crude glycerine valorization is its transformation into glycerol derivatives such as glycerol carbonate. Glycerol carbonate is a key multifunctional compound employed as solvent, fuel additive, monomer, and chemical intermediate. Due to its low toxicity, low evaporation rate, low flammability, and moisturizing ability, glycerol carbonate is used as wetting agent for cosmetics and carrier solvent for medical preparations [3].

There are several methods for the preparation of glycerol carbonate, based on the reaction of glycerol with phosgene, dialkyl carbonate or alkylene carbonate, urea, carbon monoxide and oxygen. Traditionally, cyclic carbonates have been prepared by reaction of glycols with phosgene, but due to the high toxicity and corrosive nature of phosgene, alternative routes such as transesterification reaction of dialkyl or alkykene carbonates to obtain cyclic carbonates have been explored [4-8]. The most interesting route of producing glycerol carbonate is the reaction between glycerol and urea. The main advantage of this method is that urea is a readily available and cheap reactant. In addition, ammonia formed as by-product can be easily reconverted to urea, since the urea synthesis is performed from ammonia and carbon dioxide [3].

The reaction of glycerol and urea has two major steps. The first is carbamation of glycerol by urea producing glycerol carbamate followed by the second step decomposition of carbamate resulting ammonia and glycerol carbonate. Finding the right catalyst is an important parameter. Ball et al. [9] reported the reaction between primary and secondary alcohols with urea to form alkyl carbonates can be improved using an adequate combination of a weak Lewis acid and a Lewis base. A class of catalysts that contains this feature is hydrotalcites.

This paper presents our results related to obtaining glycerol carbonate from glycerol and urea in presence of an heterogeneous catalyst. The method has been focused on glycerol carbonylation using as catalyst a zinc-aluminium hydrotalcite like compounds (Zn-Al-SO_4) with sulfate as interlayer anion.

Experimental part

Materials and methods

The following reagents and materials were used: glycerine from SC Chimreactiv srl, urea from Sigma-Aldrich, acetonitrile from Fluka, n-butylamine from Carlo Erba Reagents, zinc sulfate 7-hydrate and *aluminum sulfate 18-hydrate* from Sharlau Chemie S.A., sodium hydroxide from Lach-Ner.

Catalyst synthesis

Zinc-aluminium hydrotalcites with Zn/Al molar ratios of 3 containing sulfate as interlayer anion, was synthesized at room temperature by the coprecipitation method under low supersaturation conditions [11,12]. A mixture of 1M solutions of zinc sulfate and aluminium sulfate as precursor and a 2M solution of NaOH as precipitant were used. The resulted slurry was aged at 65°C for 30 min, filtrate, washed with deionized water until the *p*H of the filtrate was 7, and dried at 105°C for 12 h. In all the experiments described above, distilled water was reboiled to expel carbon dioxide just before its use.

Catalyst characterization

The XRD measurements were carried out using a Bruker D8 Advance, X-ray diffractometer with Cu Kα radiation

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(λCu =1.5406 A) operating at a voltage of 40 kV and a current of 40 mA. Data were collected in 2θ range from 1.0 to 70°, with a scanning rate of 0.1 deg*min^{-1}. The FT-IR measurements were performed with a Spectrometer FT-IR Tensor 27 - Bruker employing KBr pellet technique. Thermogravimetric analysis of the compounds were recorded in a TGA/SDTA 851 Mettler Toledo in the temperature range 1-700°C. Elemental analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Inductively coupled plasma atomic emission spectroscopy was recorded on a ICP-AES VARIAN Liberty 110.

The surface acidity was measured using the method described in [13]. The total acidity of the solid samples was measured by TGA analysis of adsorbed n-butylamine.

Carbonylation of glycerol with urea

The reactions were performed in a 500 mL round-bottom flask with three necks and a 90° angle adapter to connect it to a vacuum line. In a typical experiment glycerine and catalyst were placed under reaction conditions for 10 min before adding urea. The reaction mixture was stirred at a constant rate of 1200 rpm, and heated in a *magnetic stirrer hotplate* at the desired temperature. Reactions were run under a reduced pressure and in the absence of a solvent. After the reaction was completed, acetonitrile was added and the catalyst removed by filtration. The catalyst was washed with acetonitrile to remove the adsorbed products. The filtrate was concentrated under reduced pressure and the products was identified by GC–MS/MS. In all experiments the Zn-Al-SO_4 used is uncalcinated.

Conversion was calculated with respect to glycerol, while selectivity and yield were determinated on glycerol carbonate. GC–MS/MS measurements were made with an 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 detector (G3174A).

Results and discussions

Characterization of hydrotalcite-like compound Zn-Al-SO_4

The chemical composition of catalysts was established using elemental analysis, thermogravimetric analysis and inductively coupled plasma atomic emission spectroscopy. The obtained results indicated the following formula : $Zn_{0.759}Al_{0.259}(OH)_2(SO_4)_{0.188}0.53\ H_2O$.

XRD measuments

The XRD measurements of catalyst (fig. 1) exhibited sharp and symmetric peaks at low 2θ angles and broad and asymmetric peaks at higher 2θ angles which are characteristic of clay minerals possessing a layered structure and they are very similar to the pattern of natural hydrotalcite [14]. Data obtained from XRD spectrum show a typical hexagonal crystal structure in which the distance between metal cations *a* is 0.3062 nm and the thickness of cell *c* is 26.73 nm and the d_{003} is 0.891nm. To determine the crystallite size (D) Debye-Scherrer relationship was used and was calculated only for reticular plan characteristic peak (003). The value obtained of 11.260 nm can be attributed to the degree of disturbance in the structure which is influenced by the sulfate anion diameter. The result indicates a good crystallinity.

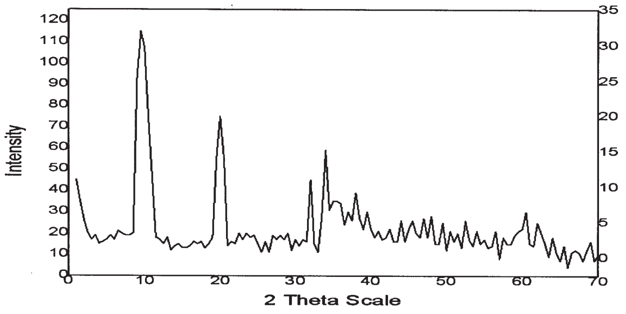

Fig. 1. XRD measurements of Zn-Al-HTC

Thermal analysis

TGA of hydrotalcite-like compound Zn-Al-SO_4 is displayed in figure 2. The sample exhibited the two characteristic steps of weight loss for hydrotalcite-like compounds [14]. A first weight loss of 5.34 % was observed from about 50 to 190 °C and is caused by the elimination of adsorbed and interlayer water. A second weight loss of approximately 13.23 % in the temperature range of 200–390 °C was caused by the loss of hydroxyl groups in the brucite layers and interlayer anion.

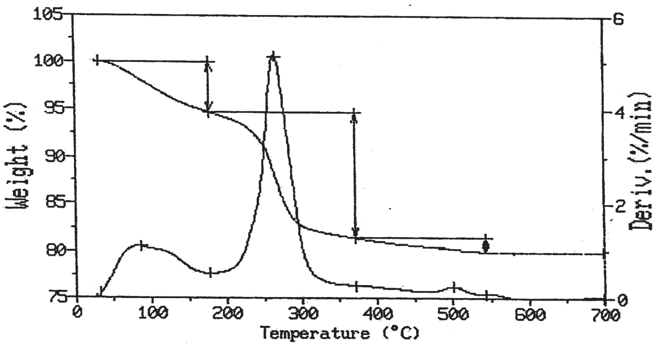

Fig. 2. Thermogravimetric analysis of Zn-Al-SO_4

FT-IR spectra

FT-IR spectrum of catalyst is presented in figure 3. Infrared spectrum of solid sample exhibit broad absorption band around 3435 cm^{-1} attributed to the stretching vibrations of hydroxyl groups present in the brucite layers. Evidence of the presence of water molecules is provided by the absorption band at 1626 cm^{-1}. The presence of sulfate anion in the compounds is indicated by the two absorption peaks at 1110 and 1188 cm^{-1}. According to the literature [15], generaly, the free sulfate symmetrical anion, being not coordinated to a metal, gives only a sharp single absorption peak at 1110 cm^{-1}. If the sulphate anion coordinates to the specified ion, the peak at 1110 cm^{-1} will be splited into 2 to 3 bands to lower the symmetry.

Acidity measurements - TGA of chemisorbed n-butylamine

The number of acid sites and their relative strengths were estimated by thermogravimetric analysis (TGA) of adsorbed n-butylamine. n-Butylamine (pKb = 3.23) was chosen because is a relatively strong base and will react better with weaker acid sites than either pyridine or ammonia.

To study the acid properties of catalyst, it was considered that the basic molecules enter the catalyst pores, to interact with all the acid sites. The number of acid sites was determined from the amount of base required to reach the saturation point [16]. Thermogravimetric analysis of catalyst (fig. 4) shows two weight losses in the temperature range of 100-150°C due to desorption of physically adsorbed water and n-butylamine. The acid strength of hydrotalcite-like compound Zn-Al-SO_4 is indicated by the third mass loss at the temperature range 200-350°C, attributed to the dissociation of the n-butylamine from medium acid sites. Acid sites density of catalyst is 1.58 meq/g .

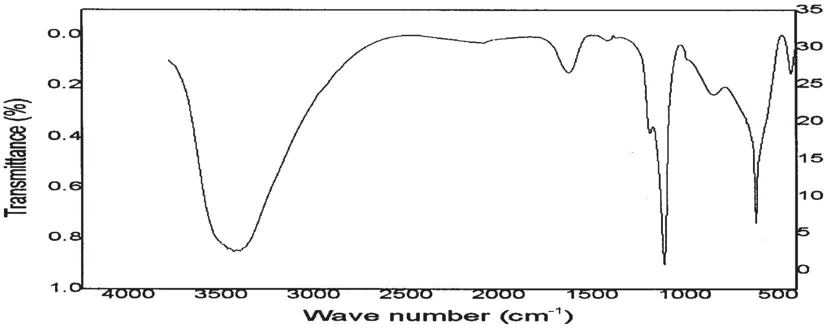

Fig. 3. FTIR spectra of Zn-Al-SO_4

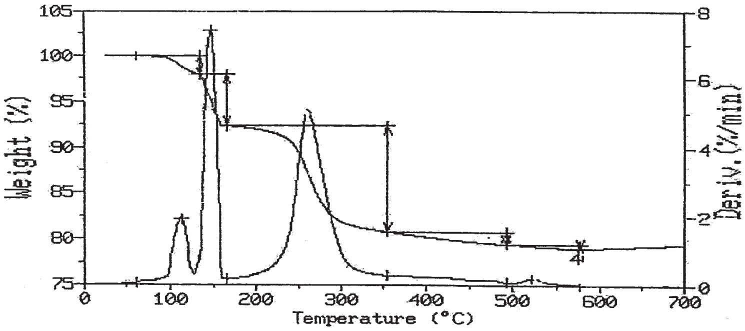

Fig. 4.TGA of chemisorbed n-butylamine

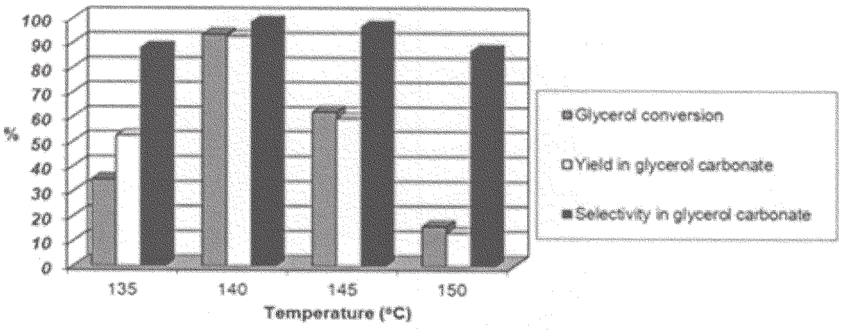

Fig. 5. Influence of reaction temperature on the catalytic performance of Zn-Al-SO_4

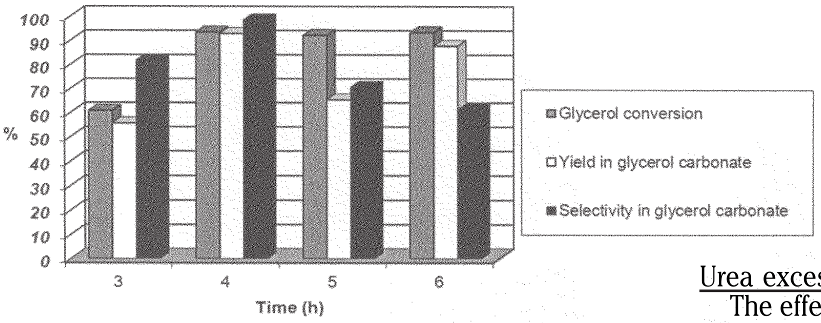

Fig. 6. Influence of reaction time on the catalytic performance of Zn-Al-SO_4

Optimization of glycerine carbonylation with urea

Reaction temperature

As shown in fig. 5, the reaction temperature has a great influence on the catalytic performance. The results show the yields in glycerol carbonate increased from 52.46 to 92.84% as the temperature rose from 130 to 140°C; however the conversions decreased after 140°C at 59.45 respectively 13.34% at 145°C respectively 150°C. The highest yield, selectivity in glycerol carbonate and glycerol conversion was reached at 140°C.

Reaction time

Another parameter that has been tested was reaction time. From the obtained data, presented in fig. 6, the reaction reached its highest yield in glycerol carbonate of 92.84 %, after 4 h. Increasing the reaction time, resulted in decreasing of the yield and selectivity, which might be due to the further decomposition of glycerol carbonate.

Urea excess

The effects of molar ratio of glycerol to urea were also measured. Obtained catalytic performance are presented in the figure 7. The best catalytic performance was recorded at a molar ratio glycerol / urea of 1:1.05. The results show that a large excess of urea leads to a decrease in glycerol carbonate yields. The reason is that the excess of ammonia and carbon dioxide resulted from the urea decomposition, reacts with each other and resulted ammonium carbonate which deposed on the vacuum pump pipelines.

Catalyst amount

Figure 8 shows the influence of the catalyst amount on the reaction performances. As can be seen, there is a strong dependence of the conversion of glycerol and the yield of glycerol carbonate on the dosage of the catalysts.

Catalytic performances of hydrotalcite increased with the increasing of catalyst amounts. Maximum yield in glycerol carbonate was achieved when 5 wt % of catalyst with respect to glycerol was used. Further increase of catalyst amount did not raise the conversion.

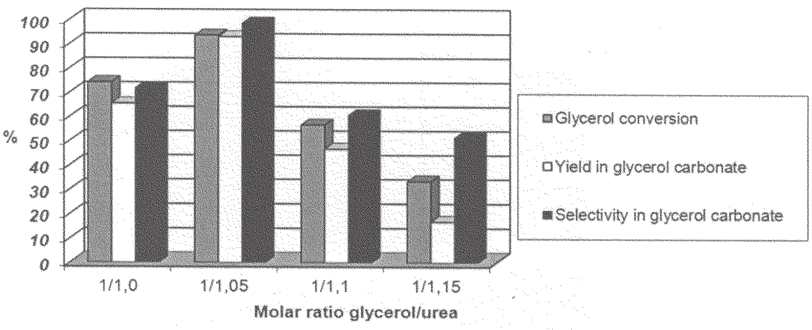

Fig. 7. Influence of molar ratio glycerol/urea on the catalytic performance of Zn-Al-SO$_4$

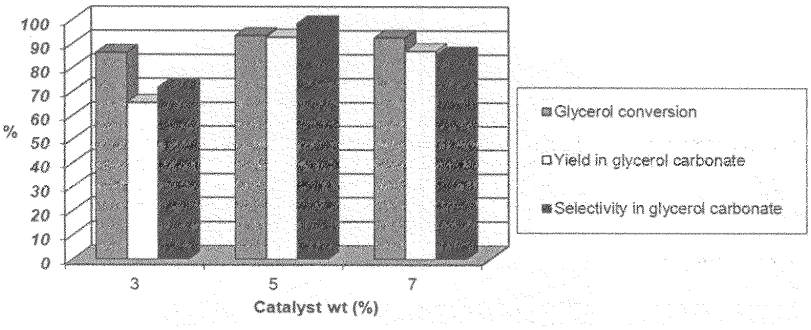

Fig. 8. Influence of catalyst quantity on the catalytic performance of Zn-Al-SO$_4$

Table 1

INFLUENCE OF Zn/Al RATIO AND ACID SITE DENSITY ON THE CATALYTIC PERFORMANCE OF Zn-Al-HTC

Entry	Molar ratio Zn/Al	Acid site density (meq/g)	Glycerol conversion (%)	Yield in glycerol carbonate (%)	Selectivity (%)
1	1	1.33	11.49	7.93	65
2	2	1.72	82	72.38	89.98
3	3	1.58	93.48	92.84	98.5
4	4	1.93	19.91	9.1	76.90

All experiments were carried out using 5 wt % of catalyst with respect to glycerol, at 60 mbar and 140°C, for 4 h and urea excess 5%.

Table 2

STUDY OF THE REUSABILITY OF Zn-Al-HTC CATALYST IN THE SYNTHESIS OF GLYCEROL CARBONATE

Entry	Cycles	Glycerol conversion (%)	Yield glycerol carbonate (%)	Selectivity (%)
1	1	93,48	92,84	98.50
2	2	92	86,22	98.50
3	3	90	86	98.45

All experiments were carried out using 5 wt% of catalyst with respect to glycerol, at 60 mbar and 140 °C, for 4 h, urea excess 5%.

Zn/Al molar ratio

Another major parameter that influences the catalytic performance is the molar ratio Zn / Al. According to the thermogravimetric analysis (TGA) of adsorbed n-butylamine (table 1), acid sites density increase with the increasing of Zn / Al molar ratio from 1.33 to 1.72 meq/g for 1 and respectively 2 Zn/Al molar ratio; after that, decreases at 1.58 meq/g for Zn/Al molar ratio of 3 and increases again at 1.93 meq/g for Zn/Al molar ratio of 4. However, yield in glycerol carbonate increase with the increasing of Zn/Al molar ratio reaching the maximum value (92.84%) at Zn/Al molar ratio at 3; after that, decrease at 9.1% for Zn/Al molar artio of 4 which has the biggest acid site density. Data obtained from experiments showed that the carbonylation reaction of glycerol with urea follows a high efficiency in the presence of a solid catalyst which has an adequate acid sites density.

Recycling catalyst

The reuse of the catalyst was investigated. To evaluate catalyst deactivation and recycling, the Zn-Al-HTC was rinsed after the first use (entry 1, table 2) with acetonitrile, air-dried and used again under exactly the same conditions (entry 2 and 3, table 2). During the experiments, the catalytic activity of hydrotalcite decreased with 6.26% from 92.48% to 86.22% , but the selectivity remained the same. The third consecutive run reached similar selectivity and yield as in the second cycle. In other words, experiments related to catalyst deactivation show a decreasing of yield after the first reuse; in the further reuses yields and catalyst activity remain at the same level.

Conclusions

The carbonylation of glycerol with urea is better carried out with heterogeneous catalysts with an adequate acid site density. The experimental results show the maximum conversion in glycerol carbonate was reached at the temperature 140°C, pressure 60 mbar, in 4 h, when Zn-Al-SO$_4$ was used as catalysts, with a ratio of 3.5 wt % with respect to glycerol, and 5 wt % stoichiometric excess of urea. The synthesized catalyst is insoluble in glycerine and glycerol carbonate, which allows to substitute the difficult recyclable ZnO or ZnSO$_4$, commonly used as catalysts in glycerol carbonate preparation.

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