



# Monitoring the catalytic synthesis of glycerol carbonate by real-time attenuated total reflection FTIR spectroscopy

V. Calvino-Casilda<sup>a,b,\*</sup>, G. Mul<sup>b</sup>, J.F. Fernández<sup>c</sup>, F. Rubio-Marcos<sup>c,1</sup>, M.A. Bañares<sup>a</sup>

<sup>a</sup> Catalytic Spectroscopy Laboratory, Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, 28049 Madrid, Spain

<sup>b</sup> Photocatalytic Synthesis Group, Faculty of Science & Technology, University of Twente, Enschede, The Netherlands

<sup>c</sup> Electroceramic Department, Instituto de Cerámica y Vidrio, CSIC, Kelsen 5, 28049 Madrid, Spain

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## ABSTRACT

*In situ* Attenuated Total Reflectance FTIR spectroscopy was used to study the carbonylation of glycerol with urea. Cobalt oxide nanoparticles,  $\text{Co}_3\text{O}_4$ , hierarchically dispersed on zinc oxide microparticles, ZnO, were used as catalysts. The present work demonstrates that *in situ* real-time attenuated total reflection ATR-FTIR spectroscopy is a valuable tool for monitoring reaction progress and analyzing the reaction mechanism of the synthesis of glycerol carbonate. ATR-FTIR spectroscopy during the carbonylation reaction of glycerol with urea reveals differences in reactivity of various  $\text{Co}_3\text{O}_4/\text{ZnO}$  catalysts, and in particular demonstrates that the first (fast) step in the conversion of glycerol with urea is the formation of glycerol urethane, whereas the consecutive conversion to glycerol carbonate is relatively slow. In addition, possible interactions of the catalytically active sites with in particular the product glycerol carbonate were also evaluated. Interactions of the 2-hydroxyethyl chain of the product with the surface of the catalysts were identified, suggesting product inhibition might be of relevance to the reaction kinetics.

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## 1. Introduction

Glycerol is a renewable and inexpensive raw chemical, which use depends on its efficient conversion to value-added materials. Particularly, glycerol carbonate and its derivatives have received increasing attention during the last years due to their potential end use as solvent and for plastics. Since renewable raw chemicals may compete with, and replace petroleum-derived ones [1–3], the need for successful routes to efficiently produce glycerol carbonate is evident. This reaction is typically run with carbonylating agents; glycerol carbonate is formed by reaction of glycerol with  $\text{CO}_2$  under supercritical conditions, or with dimethyl carbonate [4,5], or dialkyl carbonates [6] or urea [7] under milder reaction conditions. Among these, urea is a particularly attractive carbonylating agent due to the mild reaction conditions and high selectivity. Therefore, developing a heterogeneous catalyst for this process has strategic and environmental benefits.

It has been demonstrated that heterogeneous catalysts are particularly efficient for carbonylating glycerol with urea affording

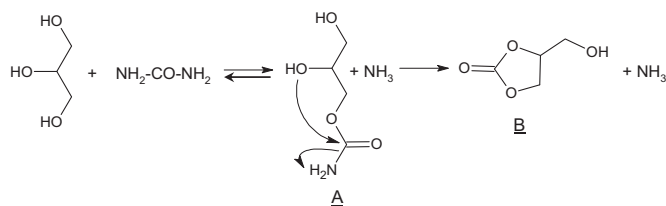
good yields under moderate reaction conditions [8,9]. Further, hierarchical nanoscaled materials dispersed on microscaled particles have been recently reported as successful catalysts for the synthesis of glycerol carbonate, affording very high yield [10]. These hierarchically dispersed materials raise additional environmental value since their synthesis is particularly clean. They are prepared by mixing oxides of different materials using a residue-free and solvent-free nanodispersion method that leads to hierarchical nano-microparticle systems [10–12]. It has been proven that after the partial reaction of two oxides, the creation of interfaces at the nanoscale range endow the catalysts with new properties that range from magnetic or optic to catalytic [10,12–15], due to proximity and diffusion phenomena.

Consistent with previous studies [7,9,10], urea reacts with glycerol when heated in the presence of a catalyst. The reaction mechanism follows four possible steps; carbamoylation of glycerol to glycerol urethane, carbonylation of glycerol urethane to glycerol carbonate with abstraction of ammonia, or carbonylation of glycerol urethane to 5-(hydroxymethyl)oxazolidin-2-one without abstraction of the ammonia. Finally glycerol carbonate can react with another molecule of urea to obtain (2-oxo-1,3-dioxolan-4-yl)-methyl carbamate, which would decrease glycerol carbonate selectivity [9,10]. Hierarchical  $\text{Co}_3\text{O}_4/\text{ZnO}$  systems are catalytically active in the synthesis of glycerol carbonate, which performance depends on the degree of interaction at the interface that is directly related to temperature treatment [10]. The nanodispersion method of preparation yields  $\text{Co}_3\text{O}_4$  active sites dispersed in the  $\text{Co}_3\text{O}_4/\text{ZnO}$

\* Corresponding author at: Catalytic Spectroscopy Laboratory, Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, 28049 Madrid, Spain. Tel.: +34 91 5854879.

E-mail addresses: [vcalvino@icp.csic.es](mailto:vcalvino@icp.csic.es) (V. Calvino-Casilda), [banares@icp.csic.es](mailto:banares@icp.csic.es) (M.A. Bañares).

<sup>1</sup> Current address: Laboratoire de Science des Procédés Céramiques et de Traitements de Surface, Université de Limoges, France.



**Scheme 1.** Reaction mechanism between glycerol and urea over  $\text{Co}_3\text{O}_4/\text{ZnO}$  catalytic systems. Reaction products: (A) Glycerol urethane (intermediate); (B) Glycerol carbonate (main product).

system. The  $\text{Co}_3\text{O}_4/\text{ZnO}$  systems prepared by dry nanodispersion at room temperature showed the best results ( $\text{Co}_3\text{O}_4$  10 wt.%: up to 69% conversion, 96% selectivity to glycerol carbonate) compared to  $\text{Co}_3\text{O}_4/\text{ZnO}$  systems preheated at  $500^\circ\text{C}$  ( $\text{ZnCo}_2\text{O}_4$  spinel inactive species were formed) [10]. A further increase in the amount of cobalt oxide (from 1 to 10 wt.%) led to an increase in catalytic activity, which is less significant for calcined samples since the spinel is the main phase present in the system [10]. Therefore, systems with a given chemical composition provide a collection of catalysts with very different catalytic performance, which can be used to study the reaction mechanism by comparison of the performance of a high- and a low-performing catalyst.

The ATR-FTIR technique is used in a wide range of applications and, recently, has been proven to be a useful tool for real-time monitoring and *in situ* studies of liquid phase reactions under working conditions (“*operando*”) [16–21]. Both reaction intermediates and species adsorbed on/or interacting with the catalyst surface can be detected. These advantages make this technique very suitable for both kinetic and mechanistic studies of heterogeneous catalyzed liquid phase reactions. This work studies both the evolution of the reaction mixture and interaction of reactants and products with the  $\text{Co}_3\text{O}_4/\text{ZnO}$  catalyst. Thus, we could study the mechanism of the formation of the glycerol urethane intermediate and that of the glycerol carbonate product (Scheme 1A and B). The surplus value of the *in situ* technique was illustrated by the fact that interactions with catalyst particles could be observed in the reaction.

## 2. Experimental

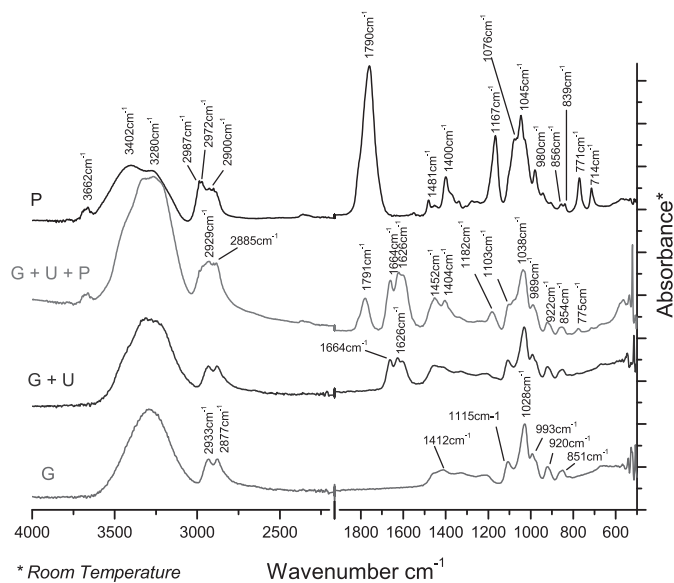
### 2.1. Preparation of the $\text{Co}_3\text{O}_4/\text{ZnO}$ catalysts

Catalysts containing 1 and 10 wt.% of  $\text{Co}_3\text{O}_4$  nanoparticles on ZnO microparticles were prepared by a well-defined dry nanodispersion procedure [10,11]. The dry dispersion process consisted on shaking  $\text{Co}_3\text{O}_4/\text{ZnO}$  mixtures and 1 mm  $\text{ZrO}_2$  balls in a  $60\text{ cm}^3$  nylon container for 5 min at 50 rpm using a tubular-type mixer. Pure ZnO and  $\text{Co}_3\text{O}_4$  powders were also subject to the same mixing process to ensure that no structural disorder contributions occur by the mixing process. Then, ZnO and  $\text{Co}_3\text{O}_4$  powders were dried at  $110^\circ\text{C}$  for 2 h before dry mixing. The resulting materials were used as prepared (room-temperature), denoted as RT-10CoZn, and calcined at increasing temperatures, up to  $500^\circ\text{C}$ , denoted as 500C-10CoZn.

The characterization of these catalysts is reported and discussed elsewhere [10], including particle size and morphology (FE-SEM and TEM) and structural features (XRD and Raman spectroscopy) of the powders.

### 2.2. ATR-FTIR experiments

ATR-FTIR experiments were performed using a Pike accessory equipped with a diamond ATR crystal coupled to a 1 mL cell containing a quartz window on the top plate. The operation conditions of the  $\text{Co}_3\text{O}_4/\text{ZnO}$  catalysts are suitable for the high-temperature ATR cell ( $145^\circ\text{C}$  reaction temperature, and urea-glycerol mixture).



**Fig. 1.** ATR-FTIR spectra of reactants; glycerol (G) and urea (U), and the product; glycerol carbonate (P).

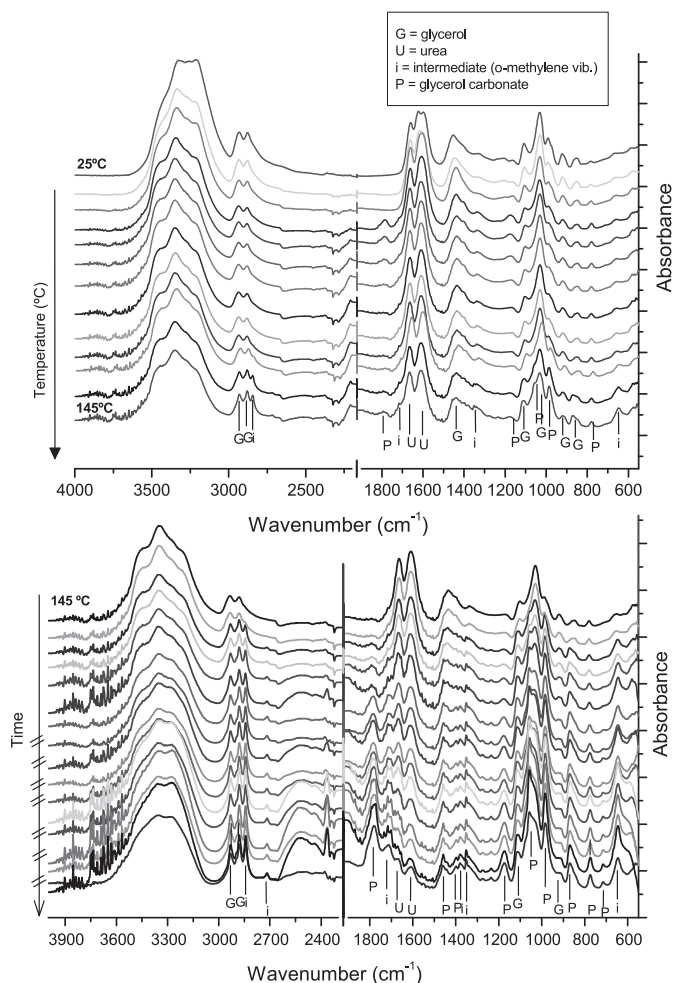
In addition, this accessory also offers a high pressure, wide spectral range and heated crystal plate.

The coating of the catalyst was carried out by suspension of the catalyst in water using a concentration of 6 wt.% of the respective  $\text{Co}_3\text{O}_4/\text{ZnO}$  mixture. The catalyst was spread on the diamond crystal and dried at  $70^\circ\text{C}$  in vacuum for 30 min. Prior to the reaction, adsorption of the reactants glycerol and urea (1:1) on the coating was monitored from room temperature to  $145^\circ\text{C}$  taking spectra during heating (heating ramp  $10^\circ\text{C}/\text{min}$ ). The FTIR spectra were registered on a Bruker Vertex 70, equipped with a liquid nitrogen cooled MCT detector. All measurements had a  $4\text{ cm}^{-1}$  resolution. When the reaction reached  $145^\circ\text{C}$ , spectra were registered every 10 min for a period of 4 h. The reaction temperature was continuously monitored by a thermocouple during experiments.

## 3. Results and discussion

Fig. 1 shows the ATR-FTIR spectra at room temperature of reactants, glycerol (G) and urea (U), the corresponding product, glycerol carbonate (P) and the mixture of reactants and product (G + U + P). The main characteristic bands of glycerol carbonate can be found at 3280, 3402 and  $1400\text{ cm}^{-1}$  due to O–H vibrations of the 2-hydroxyethyl chain of the product; 2900, 2972 and  $2987\text{ cm}^{-1}$  due to  $\text{CH}_2$  and CH vibrations of the O-methylene and O-methylidene groups of the cyclic carbonate,  $1791\text{ cm}^{-1}$  due to C=O stretching of the 5-membered cyclic carbonate; and finally 1167 and  $1045\text{ cm}^{-1}$  due to C–C, and C–O stretching respectively of the 2-hydroxyethyl chain of the product. To study the reaction, we followed the depletion of the bands corresponding to urea at 1664 and  $1626\text{ cm}^{-1}$ , which show the most well-defined changes in the spectra during reaction, besides the formation of new bands corresponding to glycerol urethane intermediate and glycerol carbonate product.

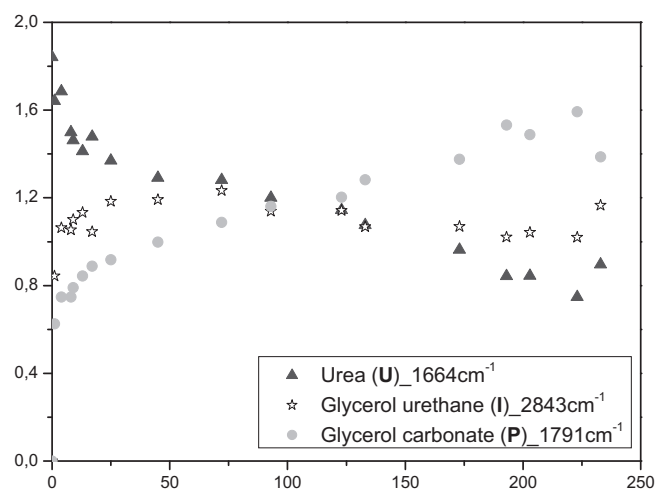
The results corresponding to the real-time ATR monitoring of the carbonylation reaction of glycerol with urea are shown below. Fig. 2 illustrates the results of the reaction of glycerol with urea at  $145^\circ\text{C}$  over room-temperature synthesized 10% $\text{Co}_3\text{O}_4/\text{ZnO}$  (RT-10CoZn) catalysts. This is the most active and selective catalyst in this series for formation of glycerol carbonate, delivering 69% conversion and 96% selectivity [10]. As the reaction temperature increases from room temperature to  $145^\circ\text{C}$  with a heating ramp of  $10^\circ\text{C}/\text{min}$  (Fig. 2, top), new IR bands corresponding to O-methylene



**Fig. 2.** ATR-FTIR spectra during heating from 25 to 145 °C (top) (heating ramp 10 °C/min) and time-resolved ATR-FTIR spectra of carbonylation of glycerol with urea at 145 °C during 4 h (spectra taken every 10 min) over RT-10CoZn systems (bottom). “//” symbol indicates a spectrum omitted due to interferences caused by the formation of ammonia bubbles.

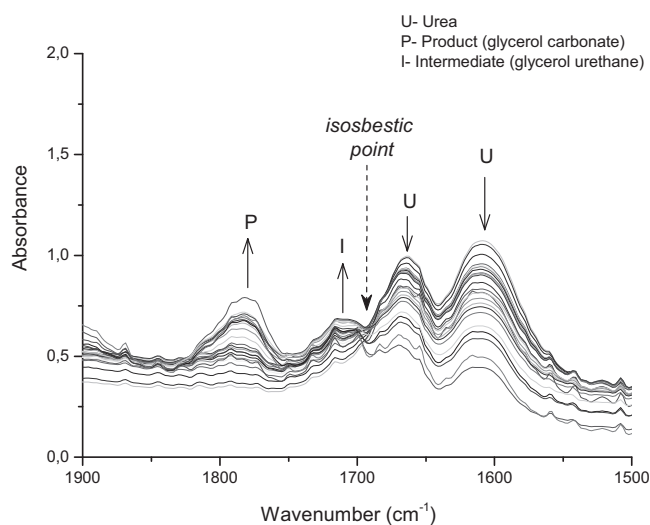
vibrations associated with the glycerol urethane reaction intermediate, (Scheme 1A) become apparent at 2843, 1716, 1352 and 644 cm<sup>-1</sup>. The formation of some characteristic bands of the glycerol carbonate product (Scheme 1B) also becomes apparent. One of the most prominent changes during the heating of the mixture were observed in the range 3700–3000 cm<sup>-1</sup> corresponding to hydroxyl vibrations in the glycerol molecule, reaction intermediate and final product. As we can observe in Fig. 2, the interaction between hydroxyl groups and cobalt active sites slightly shifts characteristic bands of hydroxyls to higher frequencies, when heating the mixture from 25 to 145 °C.

The urea bands at 1626 and 1664 cm<sup>-1</sup> decrease while the mixture is kept at 145 °C for 4 h (Fig. 2, bottom). The formation of glycerol carbonate product is also apparent, but its IR bands are less pronounced as compared to those due to glycerol urethane intermediate. Intensity changes in the 2900–2700 cm<sup>-1</sup> range due to CH<sub>2</sub> and CH vibrations, might also be affected by detachment of some catalyst particles from the diamond. This will result in changes in reflective index of the catalyst/reactant mixture at the diamond interface, and hence in the effective path for absorption [22–24]. Detachment should not affect catalysis: interactions of the catalyst particles and the diamond crystal are small, and mass transfer limitations to the catalyst coating not expected as a result of the low reaction rate.

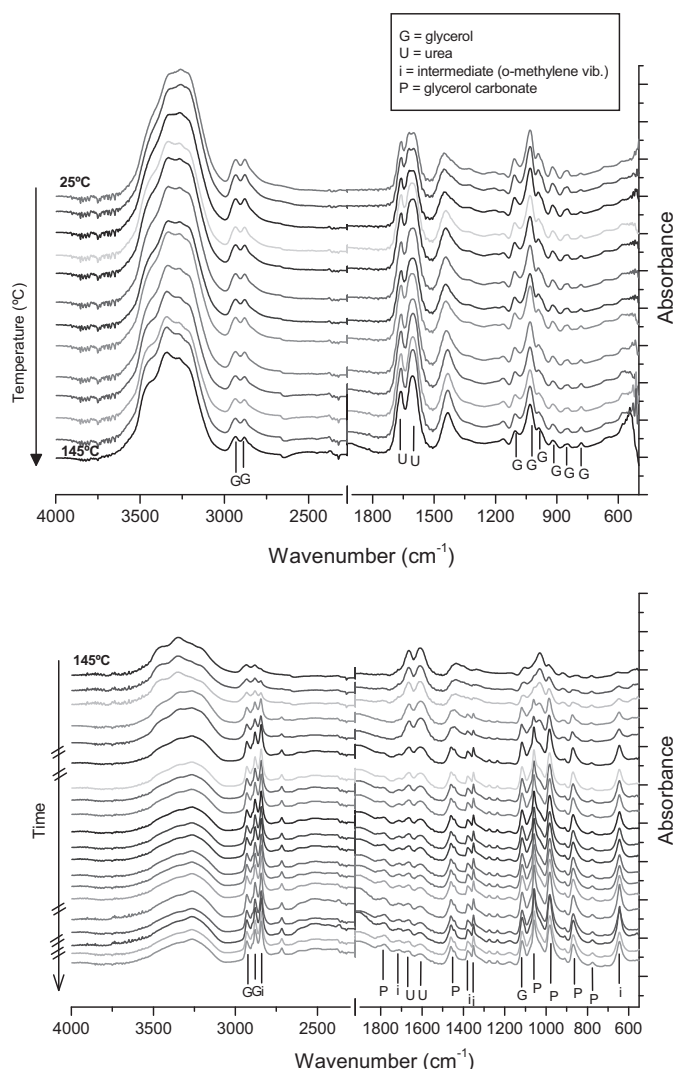


**Fig. 3.** Evolution of the intensity of representative peaks corresponding to urea (reactant), intermediate (glycerol urethane) and glycerol carbonate (product) at 145 °C on RT-10CoZn catalyst.

Fig. 3 plots the evolution during reaction at 145 °C of the most representative bands of urea (reactant) at 1664 cm<sup>-1</sup>, glycerol urethane (reaction intermediate) at 2843 cm<sup>-1</sup> and glycerol carbonate (product) at 1791 cm<sup>-1</sup>, using the RT-10CoZn catalyst. The characteristic band of urea decreases initially rapidly with reaction time, reflecting its consumption; concomitantly the band corresponding to glycerol carbonate increases with time, evidencing the formation of this reaction product. During ca. the first hour of reaction time, the characteristic band of the reaction intermediate (glycerol urethane) follows a trend similar to that corresponding to the product; thus the glycerol urethane forms quickly and then is converted rather slowly into the glycerol carbonate product. This confirms that the urethane is an intermediate in the formation of the carbonate and agrees with the mechanism suggested for this reaction [7,9]; the fast step of the reaction is the conversion of glycerol to glycerol urethane and the slow step of the reaction is the conversion of glycerol urethane to glycerol carbonate. Glycerol urethane intensity passes through a maximum with reaction time; while glycerol carbonate signal keeps on increasing with reaction time. Further insight is illustrated in Fig. 4 where the evolution of the bands



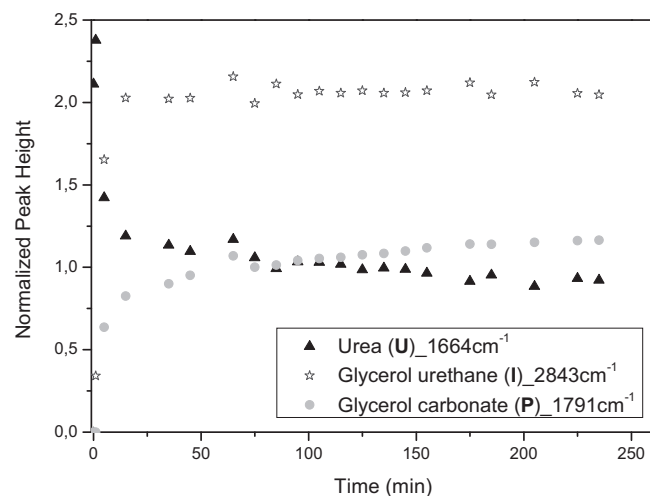
**Fig. 4.** Isosbestic point in the synthesis of glycerol carbonate from glycerol and urea at 145 °C with on RT-10CoZn catalyst. Arrows pointing up indicate increasing bands, and arrows pointing down, decreasing bands (spectra are taken every 10 min).



**Fig. 5.** ATR-FTIR spectra during heating from 25 to 145 °C (top) (heating ramp 10 °C/min) and time-resolved ATR-FTIR spectra during reaction of glycerol with urea on 500C-10CoZn at 145 °C for 4 h (spectra taken every 10 min) (bottom). “//” symbol indicates a spectrum omitted due to interferences caused by the formation of ammonia bubbles.

at 1716  $\text{cm}^{-1}$  (glycerol urethane intermediate) and at 1664  $\text{cm}^{-1}$  (urea reactant) defines an isobestic point at 1690  $\text{cm}^{-1}$ . Such an isobestic point underlines that the conversion of urea to glycerol urethane is direct, with no other reaction intermediate during this first step of reaction [10]. At 115 min time-of-reaction glycerol urethane (intermediate) begins to be fully converted into the product, however, the signal of glycerol urethane remains constant. It is an equilibrium-limited reaction due to the fast reversible conversion of glycerol and urea to glycerol urethane [25]; glycerol urethane will be present (and monitored) as long as ammonia remains in solution. Thus, a combination of  $\text{NH}_3$ -limiting conditions and of a slow second reaction step to form the carbonate would account for the presence of glycerol urethane intermediate for such a prolonged period after the initial rapid concentration changes.

Fig. 5 shows ATR-IR spectra during the reaction of glycerol with urea over high-temperature calcined, 500C-10ZnCo, catalysts. We have reported that this catalyst is less active, but very selective, (37% conversion, 98% selectivity) for the reaction due to the formation of spinel inactive species  $\text{ZnCo}_2\text{O}_4$  [10], which decreases the number of active sites. When the reaction temperature increases from room temperature to 145 °C (Fig. 5, top) no new bands become



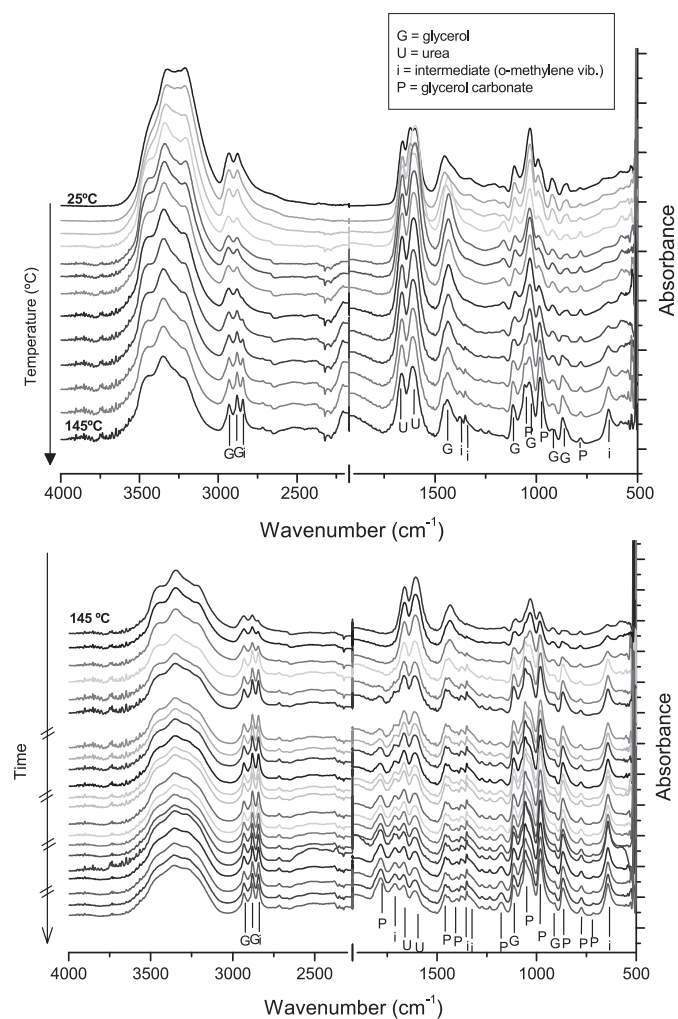
**Fig. 6.** Evolution of the intensity of representative peaks corresponding to urea (reactant), glycerol urethane (intermediate) and glycerol carbonate (product) during reaction at 145 °C on using the 500C-10CoZn catalyst.

apparent; only those corresponding to glycerol and urea reactants are present, indicating that no reaction occurs. New bands corresponding to the reaction intermediate (glycerol urethane) and the glycerol carbonate product appear when the temperature was kept at 145 °C during 4 h (Fig. 5, bottom). With reaction time, most bands grow sharper, again the result of detachment of the particles from the crystal. Fig. 6 illustrates the evolution of representative peaks corresponding to urea (reactant), glycerol urethane (intermediate) and glycerol carbonate (product) using the 500C-10CoZn catalyst. The intensity of the representative band of urea decreases more rapidly during the first 80 min of reaction and levels off. The characteristic band of the urethane intermediate grows quickly and quite in parallel to that of the carbonate product, which means that glycerol urethane is formed and fully converted into the product. Unlike on RT-10CoZn, urethane signal does not decrease and that of the carbonate does not grow with reaction time. The IR bands corresponding of hydroxyl groups are significantly less shifted to higher frequencies on 500C-10CoZn than on RT-10CoZn; this is indicative of a weaker interaction of these groups with the catalytic surface.

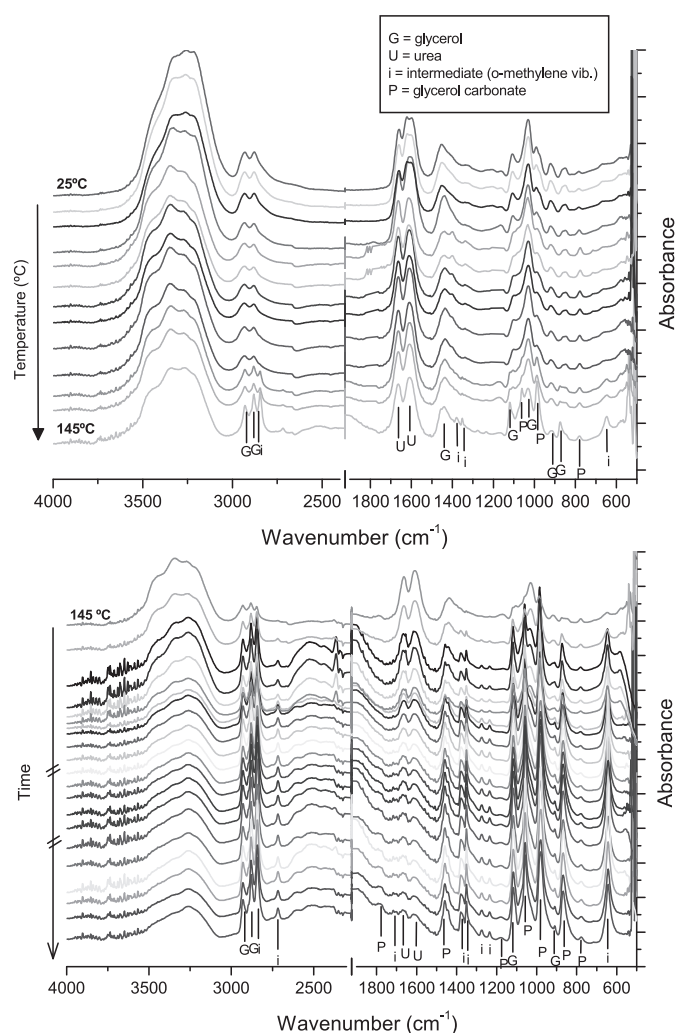
Glycerol carbonate synthesis on  $\text{Co}_3\text{O}_4/\text{ZnO}$  depends on cobalt oxide loading. Low loading catalyst, 1% $\text{Co}_3\text{O}_4/\text{ZnO}$ , prepared at room temperature (RT-1CoZn) is half as active as the one containing 10% $\text{Co}_3\text{O}_4/\text{ZnO}$  (RT-10CoZn), but it is highly selective to glycerol carbonate (35% conversion, nearly 100% selectivity) [10]. Figure 7 shows the ATR-FTIR results during reaction on RT-1CoZn. New bands due to O-methylene vibrations corresponding to glycerol urethane (Scheme 1A) and to glycerol carbonate (Scheme 1B) develop when the reaction temperature increases from room temperature to 145 °C (Fig. 7, top) shows the rapid formation of new bands corresponding to O-methylene vibrations of glycerol urethane (Scheme 1A) and also the formation of some characteristic bands of the product glycerol carbonate formation (Scheme 1B). The sharpening of several bands in the spectra suggests the formation of a reactants-products-catalyst suspension. Fig. 7 illustrates that the hydroxyl vibrations frequency shifts to higher frequencies. The lower the amount of  $\text{Co}_3\text{O}_4$  used in the preparation of the catalysts, the lower the number of cobalt active sites in its structure.

Fig. 8 shows the evolution during reaction of the representative urea, glycerol urethane intermediate and glycerol carbonate product bands. It seems that the formation of the product occurs gradually but not as fast as in the case of RT-10CoZn catalysts due to a lower number of active sites. This is consistent with lower activity recorded by off-line gas chromatography analyses. The urethane

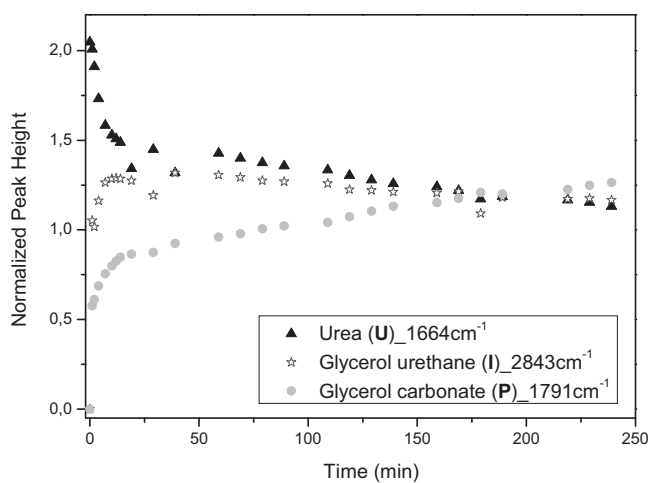




**Fig. 7.** Time-resolved ATR-FTIR spectra of the reaction of glycerol with urea on RT-1CoZn during: (top), heating from 25 to 145 °C (heating ramp 10 °C/min); and (bottom), time-resolved ATR-FTIR spectra at 145 °C for 4 h (spectra taken every 10 min). “//” symbol indicates a spectrum omitted due to interferences caused by the formation of ammonia bubbles.



**Fig. 9.** ATR-FTIR spectra during heating from 25 to 145 °C (top) (heating ramp 10 °C/min) and time-resolved ATR-FTIR spectra during reaction of glycerol with urea on 500C-1CoZn at 145 °C for 4 h (spectra taken every 10 min). “//” symbol indicates a spectrum omitted due to interferences caused by the formation of ammonia bubbles.

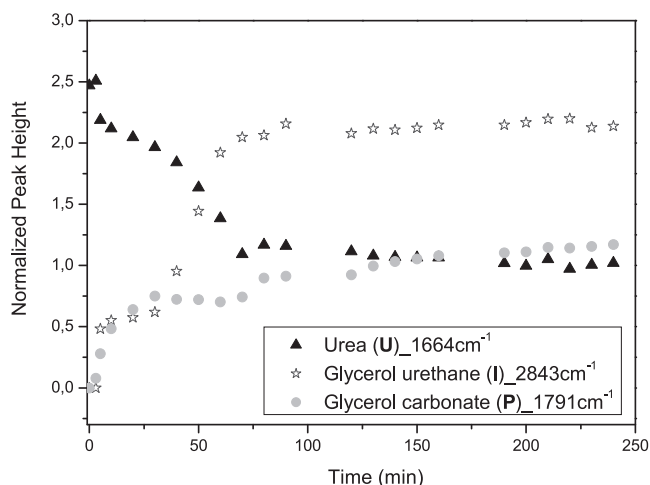


**Fig. 8.** Evolution of the intensity of representative peaks corresponding to urea (reactant), glycerol urethane (intermediate) and glycerol carbonate (product) using RT-1CoZn during reaction at 145 °C.

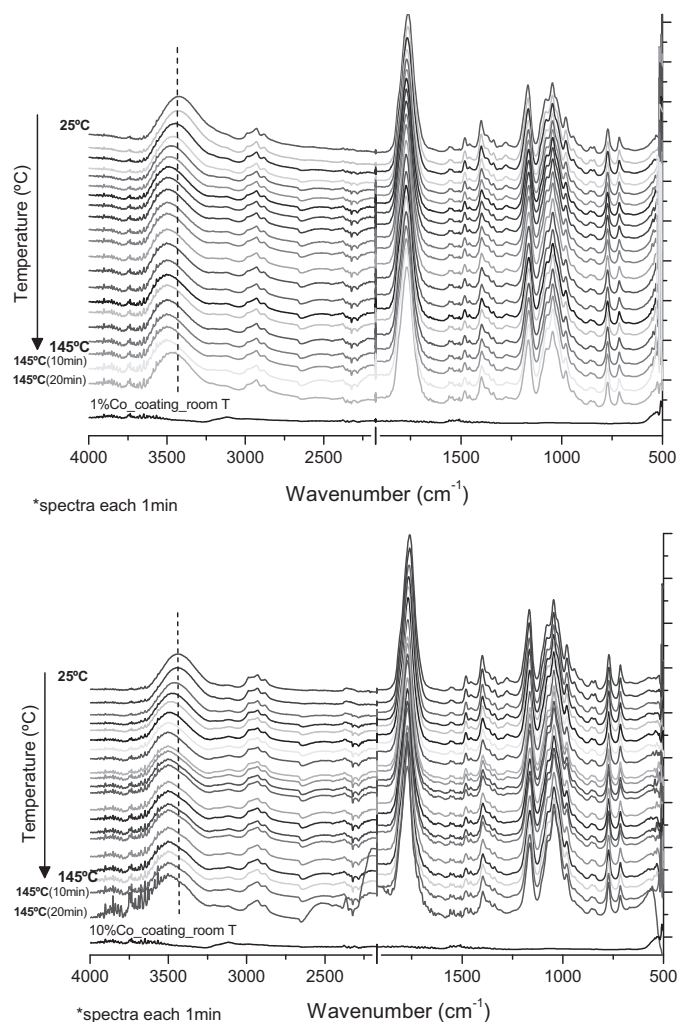
intermediate develops at 5 min reaction time, and then follows the same trend than for urea in a similar way as for RT-10CoZn.

Fig. 9 shows the performance of the 500C-1CoZn, which possess the  $\text{ZnCo}_2\text{O}_4$  spinel phase and exhibits low performance (26.8% conversion, 82.8% selectivity). This plot shows that most of the bands are sharper, this would be indicative of the formation of a suspension of 500C-1CoZn particles. Comparison of Fig. 2 (up), Fig. 5 (up), Fig. 7 (up) and Fig. 9 (up) shows that during heating of the mixture with the catalysts prepared at room temperature (RT-10CoZn and RT-1CoZn), the product appears quickly. In case of catalysts calcined at 500 °C, this is less intense. In addition, hydroxyl vibrations in the 3700–3000  $\text{cm}^{-1}$  range shows that their interaction with the active sites clearly depends on the catalyst used.

Glycerol urethane slowly forms during the first hour of reaction at 145 °C (Fig. 10), then increases quickly and levels off after 100 min of reaction time. During these 100 min of reaction, glycerol urethane is slowly converted into the product remaining in the solution, which would explain the lowest selectivity obtained by off-line gas chromatography analyses. The remarkable change observed in the glycerol urethane band trend is related to the low interaction of reactants with the surface of the catalyst, due to the presence of the spinel phase.



**Fig. 10.** Evolution of the intensity of the most representative peaks corresponding to urea (reactant), glycerol urethane (intermediate) and glycerol carbonate (product) during reaction on 500C-1CoZn at 145 °C.



**Fig. 11.** Time-resolved ATR-FTIR spectra of glycerol carbonate supported on Co-ZnO systems during heating from 25 to 145 °C on RT-1CoZn (top) and RT-10CoZn (bottom).

ATR-FTIR spectra during carbonylation of glycerol with urea suggest a possible interaction between the cobalt active sites and glycerol molecules. It seems that glycerol interacts first with the catalyst surface and then urea reacts with glycerol. Fig. 11 studies the possible interaction between glycerol carbonate product and the catalyst surface during heating from room temperature to 145 °C. This plot suggests that the band corresponding to OH vibrations shifts to higher frequencies due to interactions of the 2-hydroxyethyl chain of the product with the surface of the catalysts. Besides the aforementioned reasons for the observed trends in concentration profiles, additionally product inhibition of the reaction, induced by the relatively strong interaction of glycerol carbonate with the surface, might contribute to relatively slow conversion rates after the initial high rate of reaction. Detailed kinetic modelling is necessary to further reveal the kinetically relevant steps in the process, which is beyond the scope of the present study.

These results show that ATR-FTIR spectroscopy is a convenient technique to monitor chemical reactions, like the synthesis of glycerol carbonate and that ATR-FTIR spectroscopy may also provide real-time feedback for process control.

#### 4. Conclusions

*In situ* attenuated total reflectance FTIR spectroscopy was used to investigate the reaction pathway of glycerol to glycerol carbonate via carbonylation of glycerol urethane. To carry out these experiments hierarchical  $\text{Co}_3\text{O}_4/\text{ZnO}$  catalysts were deposited on a diamond internal reflection element incorporated in a heated base plate, and the reaction carried out in a home made liquid cell. The present work demonstrates that ATR-FTIR spectroscopy is a powerful tool for assessing the reaction progress and to investigate the reaction mechanism, while the technique is non-invasive.

Real-time ATR-FTIR monitoring during reaction provides thorough molecular information on the reaction mechanism and possible intermediates and formation of co-products. It is possible to see progressive dry media reaction of glycerol with urea. This methodology can be applied to an unlimited number of processes. Thus, this methodology is critical to understand reaction mechanisms of any organic reaction and provides a tool for real-time reaction monitoring and reaction control.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.09.036.

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