Valorization of bio-glycerol: New catalytic materials for the synthesis of glycerol carbonate *via* glycerolysis of urea

Michele Aresta [a,*], Angela Dibenedetto [a], Francesco Nocito [a], Carla Ferragina [b]

[a] Dipartimento di Chimica and CIRCC, University of Bari, Campus Universitario, 70126 Bari, Italy
[b] Istituto di Metodologie Inorganiche e dei Plasmi (IMIP)-CNR Roma 1, via Salaria km 29,300, 00016 Monterotondo (Roma), Italy

A B S T R A C T

The glycerolysis of urea plays an important role in the conversion of glycerol into glycerol carbonate because it is a phosgene-free process that uses easily available and low-cost raw materials that have a low toxicity. γ-Zirconium phosphate shows a good activity as catalyst as it affords 80% of conversion of glycerol under mild reaction conditions. The catalyst is easily recoverable and reusable in subsequent cycles of reaction.

The kinetics of the reaction has been studied considering the full parameter space. The best temperature is 418 K, with 3 h of reaction using an equimolar amount of the two reagents (glycerol and urea) with a catalyst load of 0.6–1.5% w/w with respect to glycerol. The behaviour of the catalyst has been investigated by using the TPD technique. Multinuclear ^{1}H and ^{13}C NMR and FTIR have been used for the characterization of intermediates and by-product. The reaction mechanism is fully elucidated.

1. Introduction

Glycerol (**1,** Scheme 1) is the by-product with the largest economic impact in the modern oleochemical industry [1], being formed in different processes such as glycerides transesterification, alcoholysis, hydrolytic cleavage under pressure and saponification with alkalies [2,3]. It is also produced by dedicated processes such as the synthesis from propene [4] or the fermentation of simple sugars [5]. The production of biofuels and biolubricants from biomass is much expanding (and will continue to grow) so that the production of bio-glycerol, in the past considered of great value for a successful closing of the economic balance of the lipid-utilization process, is now exceeding the request.

The risk that large amounts of glycerol are produced and will accumulate as a waste has speed-up the industry and academia research towards the identification of new opportunities for using such by-product either directly (as fuel even in the same biodiesel production plants [6]), or by converting it into useful derivatives. The latter option finds several new applications for the production of improvers of the cetane number (additives to diesel fuels: i.e. tertbutyl ether of glycerol) [7] or intermediates in the production of fine chemicals (e.g. dihydroxyacetone, glyceric acid, pyruvic acid and 1,3-propanediol) either by fermentation [8–10] or using chemical routes [11] (Scheme 1). Glycerol carbonate (**3,** Scheme 1) represents an important derivative of glycerol that shows low

toxicity, good biodegradability and high boiling point. For its properties it finds several applications in different industrial sectors, especially as a polar high boiling solvent or intermediate in organic syntheses (i.e. monomer in the synthesis of polycarbonates and other polymeric materials in the plastic field [12]), as a precursor in biomedical applications and as a protection group in the carbohydrates chemistry. It is also used as a component in membranes for gas separation, in the synthesis of polyurethanes [13] and in the production of surfactants [14].

The commonly used routes to glycerol carbonate are the reaction of glycerol with phosgene [15] and its transesterification with other carbonates [16a,b] (Scheme 2).

More recently, the direct carboxylation of glycerol with carbon dioxide (Scheme 2 middle part) has been discovered [17a–c], an interesting reaction that converts two wastes into an added value product. Such reaction requires an improvement of the catalyst in order to find a practical application.
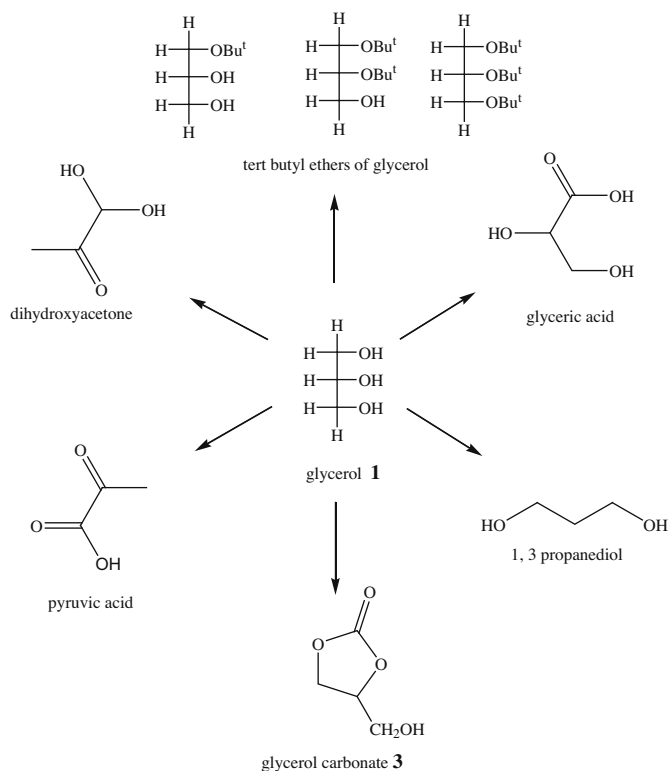
An alternative route is the glycerolysis of urea (Scheme 3), a reaction that has been recently described in the scientific [18] and patent literature [19–21].

Several catalysts have been used, mainly based on metal oxides of variable basicity [18–21] which suffer the drawback of a difficult separation from the reaction medium as they dissolve in it or are converted into micro-powders. As matter of fact, the scientific and patent reports often do not describe the recovery of the pure carbonate from the reaction mixture.
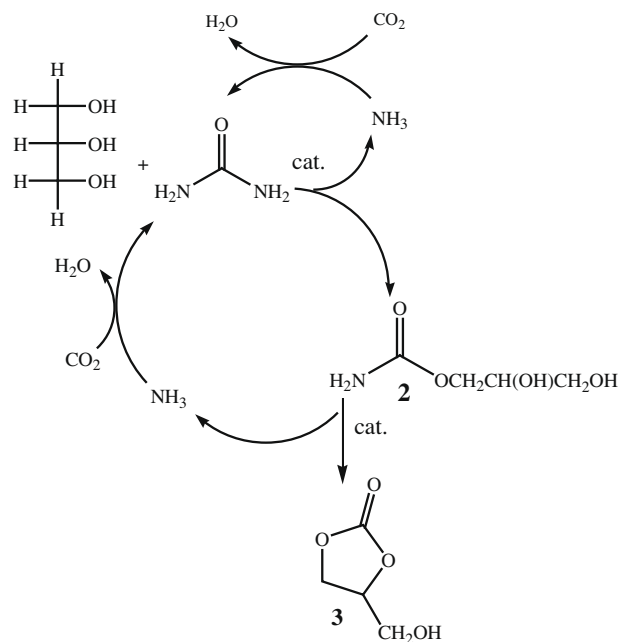
We searched and tested several catalysts which do not dissolve in the reaction mixture (glycerol–urea–glycerol carbonate) nor are

* Corresponding author. Fax: +39 080 544 36 06.
E-mail address: m.aresta@chimica.uniba.it (M. Aresta).

Scheme 1. Some derivatives of glycerol of industrial interest.

Scheme 2. Synthesis of glycerol carbonate by phosgenation (upper part), direct carboxylation (middle part) or transesterification of glycerol (lower part).

Scheme 3. Synthesis of glycerol carbonate by glycerolysis of urea.

pulverized upon stirring the reaction mixture. During our studies we identified an excellent catalytic material, easily recoverable and recyclable, and developed a process for a selective conversion of glycerol into glycerol carbonate and an easy recovery of the latter [22].

In this paper we discuss the behaviour of such catalyst and the influence of the reaction parameters on the yield and selectivity of the conversion of glycerol into glycerol carbonate.

2. Experimental

2.1. General

Chemicals were purchased from Aldrich (RP). Glycerol was re-agent grade stored out of the contact with air in order to limit the water uptake. Alternatively, glycerol recovered from the meth-anolysis of lipids in the absence of water in our laboratory was used. Solvents were further purified, distilled and stored under dinitrogen over anhydrous calcium sulphate [23]. Urea was re-duced to a fine powder before the use in the reaction. γ-ZrP was synthesized as reported in [25,22]. The infrared spectra were ob-tained through a spectrometer SHIMADZU IR Prestige 21 placing the sample between KBr disks, neat or dispersed in Nujol. The reaction liquid and/or gas products were analyzed using a gas chromatograph HP 6850 series equipped with a capillary column ZB-WAX (30 m × 0.25 mm) and with a flame ionization detector. Glycol tetraethylene dimethyl ether was used as internal standard.

The gas–mass analyses were conducted with a GC–MS SHIMADZU QP5050 equipped with the same column as the gas-chromatograph.
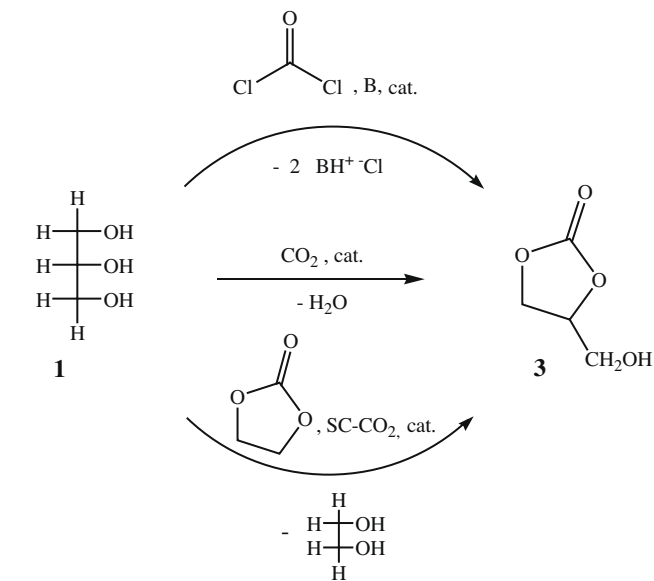
The ^1H NMR and ^{13}C NMR spectra were recorded using a VAR-IAN 400 MHz or a Bruker 600 MHz, as specified.

Acid and basic sites determination and thermal analyses on the catalysts were performed using a Micromeritics Chemisorb 2750.

The pressure in the reaction vessel was monitored using a EBRO Vacumeter VM 2000-Ex.

2.2. The catalysts used in this work

In this work we used the catalysts listed in Table 1 that presents their performance and some of their properties. The ratio of acid/basic sites, for some selected catalysts, is reported in Table 2. As re-ported in Table 1, several of the catalysts, namely compounds itemized 2–6, are not active or dissolve in the reaction medium converting into species that are difficult to characterize and isolate [25]. Therefore, species 2–6 and 9 will not be further discussed in this paper. Only a few catalysts were able to maintain their struc-ture intact during at least one catalytic run, namely titanosilicalite

Table 1
Glycerolysis of urea using several catalytic systems.[a]

Entry	Catalyst[a]	n gly/n ur[b]	w cat/w ur (%)[c]	Recovered	Conversion (%)[d]
1	None	2	Na	–	28
2	Alloy Al–Ce–Ga	2	5	Yes	30
3	TiO_2	2	5	No	32
4	CeO_2	2	5	No	32
5	Rh(diphos)BPh$_4$[e]	2	3	Yes	35
6	Bu$_2$SnO	2	5	No	36
7	Titanosilicalite	1	3	Partially	36
8	Titanosilicalite	2	3	Partially	58
9	Bi_2O_3	2	5	No	42
10	ZnO	2	3	No	48
11	γ-ZrP Zn	2	3	Yes	62
12	γ-ZrP not calcined	1	1	Yes	60
13	γ-ZrP not calcined	2	1	Yes	68
14	γ-ZrP calcined	1	1	Yes	76

[a] Reaction carried out at a temperature of 413 K, a pressure of 20 Pa to facilitate the removal of ammonia and for a time of 3 h.
[b] Molar ratio.
[c] Weight ratio.
[d] ±3% after distillation and referred to urea.
[e] Ref. [26b].

Table 2
Acid/basic sites for some catalysts used in this work.

Sample	V_{NH3} adsorbed mL/g	Total acid sites mmol/g	V_{CO_2} adsorbed mL/g	Total basic sites mmol/g	Ratio acid/basic sites
Freshly prepared γ-ZrP	33.3	1.49	3.98	0.18	8.45
Fresh γ-ZrP after 2 h calcination at 773 K	3.16	0.141	0.826	0.034	4.15
γ-ZrP after five catalytic cycles	4.29	0.19	3.96	0.176	1.08
Ti-silicalite	1.78	0.079	0.83	0.037	2.14

and γ-ZrP. The former was slowly transformed after a few runs, while the latter could be recovered and recycled several times. We shall concentrate our attention on γ-ZrP, and its properties and behaviour will be described in detail.

2.3. Techniques used for the characterization of the catalysts

The catalysts were characterized before and after their use by means of TPD techniques. FTIR was less informative. The former allowed to determine the acid/basic sites ratio and how such ratio was modified during catalysis. In particular, γ-ZrP was analyzed by TPD after its preparation, after calcination at 773 K for two hours and after one or more catalytic cycles. Table 2 shows how the properties change during operation.

Ammonia gas (preferred to pyridine as NH_3 is the real gas released during the reaction) and carbon dioxide were used as the probe molecules in the determination of the acid and basic sites of the catalysts, respectively. About 100 mg of freshly prepared γ-ZrP was placed in the quartz sample tube of the Micromeritics apparatus and pre-treated by flowing nitrogen at 773 K for 2 h. Then, the sample was cooled to 273 K (using a ice/water bath) and the chemisorption of a given probe gas was performed using helium as carrier gas. Once the sample was saturated, the TPD experiment was started with a heating rate of 10 K/min under helium flow (20 mL/min). Typical curves of release of NH_3 from γ-ZrP under different conditions are shown in Fig. 4. The results are discussed in Section 3.

2.4. Catalytic runs

Catalysis was performed in a glass reactor that allowed to monitor the changes in the reactive system. The influence of both the pressure in the vessel and the temperature on yield and selectivity was investigated. The temperature was controlled with the help of a thermostatic liquid, while the pressure was monitored with an electronic pressure gauge. Vacuum was applied with a membrane vacuum pump. When the reaction was carried out under ambient pressure, NH_3 released in the reaction was extracted with a flow of N_2 that was eventually passed through an acid water solution kept at 275 K. This allowed to titrate the released and captured ammonia. Some specific examples are reported below.

2.4.1. Glycerolysis of urea at low pressure using γ-ZrP as catalyst

The catalyst was preliminarily calcined for 3 h at 773 K. 5.1095 g of glycerol (55 mmol), 3.3033 g of powdered urea (55 mmol) and 0.0302 g of catalyst were placed in the reactor. A vacuum system (20 Pa) for the removal and capture of ammonia during the reaction was connected to the head of the reactor. The reaction was allowed to proceed for 3 h (optimum time, see below) at 418 K under stirring after which the reactor was cooled to room temperature and N_2 admitted. Glycerol carbonate was extracted using a solvent in which neither glycerol nor urea was soluble [22] and analyses were performed by gas-chromatography, GC–MS, FTIR and NMR on the extracts. The conversion of glycerol into glycerol carbonate was equal to 80%. The isolated carbonate was distilled in *vacuo* to afford 76% of the pure compound as a colourless liquid.

2.4.2. Glycerolysis of urea at 0.1 MPa

When the glycerolysis of urea was carried at 0.1 MPa in order to eliminate the formed NH_3 a flow of N_2 was passed through the reactive system and then through a water acid (1 M HNO_3) solution kept at 275 K. The trapped ammonia was determined by excess acid titration that allowed to monitor the reaction and evaluate the degree of advancement. Alternatively, the formed glycerol carbonate was extracted using a non miscible (with glycerol) solvent and quantified by GC–MS. The two data
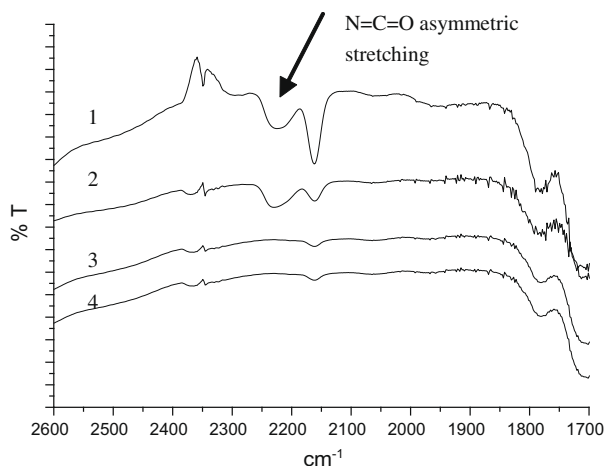
Fig. 1. FTIR spectra of the urea–glycerol mixture (after 30 min reaction) in the presence of various catalysts: (1) ZnSO$_4$; (2) ZnO; (3) Titanosilicalite; (4) γ-ZrP.

Fig. 3. Difference of trend of the yield of carbonate formation in consecutive cycles with: (i) catalyst recovered and treated thermally after two cycles (upper); (ii) consecutive additions of equimolar amounts of urea and glycerol without catalyst recovery (lower).

(titration of NH$_3$ and amount of glycerol carbonate formed) were compared and shown to be in good agreement (less that 5% discordance).

2.4.3. Glycerolysis of urea in dependence of time

Using the same procedure reported in Section 2.4.1 or 2.4.2 the reaction of glycerol and urea was performed with or without catalyst for 1, 2, 3, 4 and 5 h. At the end of each time interval, the mixture was cooled and analyzed by gas-chromatography. Yields are reported in Fig. 9.

2.4.4. Glycerolysis of urea at different temperatures

The reactor containing glycerol, urea and the pre-treated catalyst (as reported in Section 2.4.1) was heated at 380, 390, 400, 410, 420 or 430 K for 3 h under constant stirring (650 rpm), while the ammonia formed during the reaction was removed *in vacuo*. At the end of each reaction, the mixture was cooled to room temperature, the carbonate was extracted and analyzed by gas-chromatography. Yields are reported in Fig. 8.

2.4.5. Incipient reaction of urea with various catalysts

A sample was prepared by mixing in a Sovirel tube a given catalyst (ZnSO$_4$, ZnO, titanosilicalite or γ-ZrP) and urea in a 1:1 molar ratio, as in the synthesis of glycerol carbonate. The reaction was carried out for 30 min at 415 K in the closed Sovirel tube. Then the Sovirel tube was cooled to room temperature and a drop of
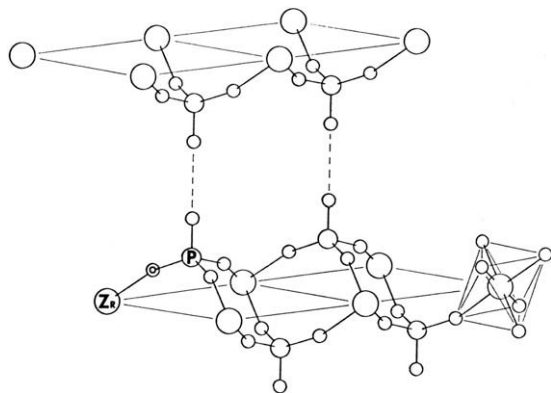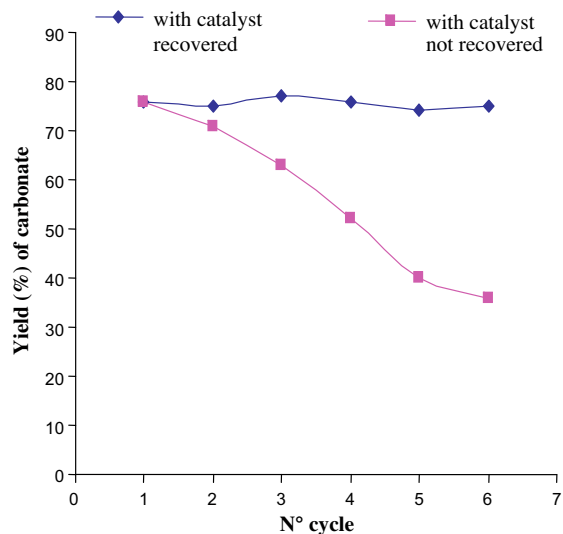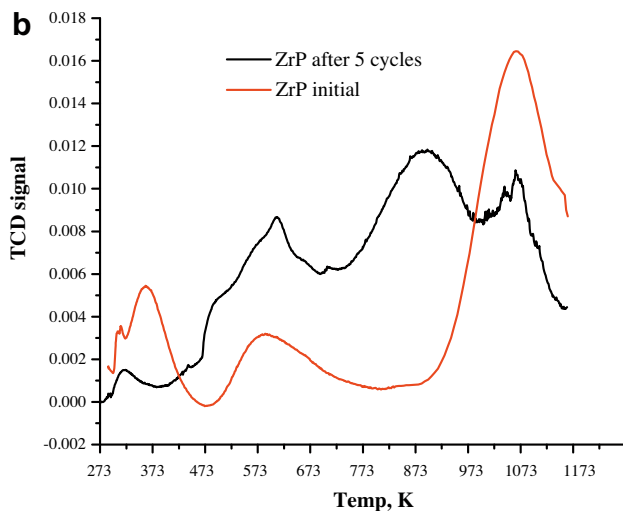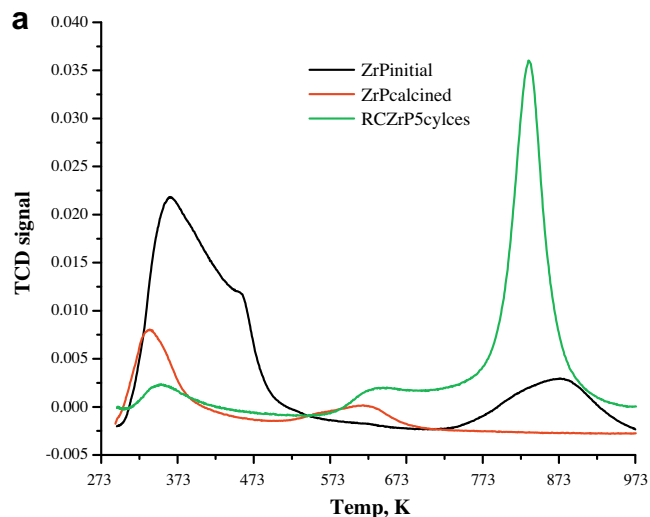

Fig. 2. Essential structural features of γ-ZrP.

Fig. 4. (a) TPD profiles for NH$_3$ release from different samples of γ-ZrP; (b) TPD profiles for CO$_2$ release from different samples of γ-ZrP.
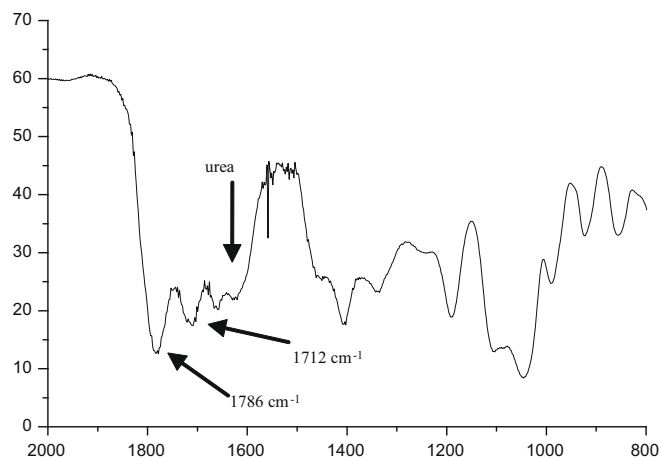
Fig. 5. IR spectrum of the reaction solution after 1 h of the first cycle (1786 cm^{-1}: carbonyl stretching of glycerol carbonate; 1712 cm^{-1}: carbonyl stretching of the carbamate, 1670 and 1620 cm^{-1}: urea).

the solution was placed between two KBr disks and analyzed by FTIR. The spectra are shown in Fig. 1.

2.4.6. Recyclability of γ-ZrP

γ-ZrP was not soluble in the reaction mixture and could be quantitatively recovered at the end of the reaction by simple decantation of the liquid and washing of the solid with CH$_3$CN or CH$_2$Cl$_2$. The recovered catalyst was calcined at 773 K for 1 h and reused. It maintained the same performance for several cycles (See Fig. 3, upper curve) Alternatively, after a cycle of 3 h of reaction, glycerol and urea were added to the reactive mixture keeping the catalyst in the reaction liquid. The selectivity of the reaction decreased but the conversion yield of glycerol was constant (See Fig. 3, bottom curve).

2.5. Analytical techniques used for the identification of species in solution and the quantification of the products

The carbamate formed in the first step of the reaction and the carbonate end-product, as well as the only by-product formed in the glycerolysis of urea, were characterized and monitored by using either multinuclear NMR (^{1}H or ^{13}C) or GC–MS techniques. Some examples of application are reported below.
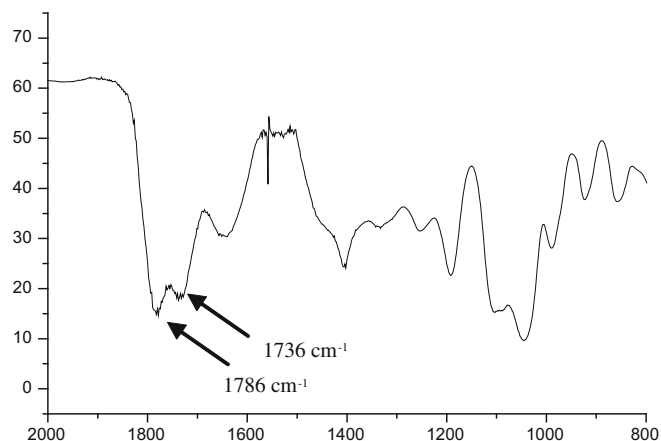

Fig. 6. IR spectrum of the reaction solution after the 5th cycle (1786 cm^{-1}: carbonyl stretching of glycerol carbonate, 1736 cm^{-1}: carbonyl stretching of the by-product).
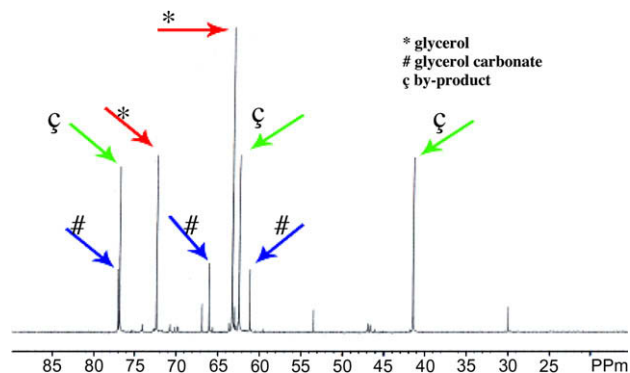

Fig. 7. {^{1}H}–^{13}C NMR (100 MHz, in CD$_3$OD) spectrum of the reaction solution after the 5th cycle and extraction of the formed carbonate: the mixture is essentially formed by three species, i.e. glycerol (*), residual glycerol carbonate (#) and the by-product (ç).

2.5.1. NMR analysis on the intermediate linear carbamate

The reaction between glycerol and urea was performed at 418 K for 30 min as described in Section 2.4.1. At the end of the reaction time, the mixture was cooled and analyzed by ^{13}C NMR in deuterated methanol. The presence of three ^{13}C NMR signals at 61, 65 and 70 ppm confirmed that the reaction between glycerol and urea took place at one of the terminal –OH group of glycerol affording the carbamato-species **2** shown in Scheme 3 more than at the C2– OH.

2.5.2. NMR analysis on the reaction mixture after five cycles of reaction

Glycerol (5.0945 g) (55 mmol) and 3.3501 g of urea (55 mmol) were reacted at 418 K in the presence of 0.0311 g of γ-ZrP for 3 h. The formed carbonate was determined by GC–MS and then separated by extraction with a solvent not miscible with glycerol. Urea and glycerol in a 1:1 molar ratio were added and the reaction was continued for 3 h. The cycle was repeated five times. After five cycles of reaction, the reaction mixture was cooled to room temperature, the carbonate was extracted and the catalyst was separated by filtration. The extracts were combined. The solvent was evaporated *in vacuo* at room temperature and the residual viscous liquid was analyzed by NMR, preparing a solution of a part of the sample in deuterated methanol. The results are shown in Fig. 7.

3. Results and discussion

3.1. Studies on the reaction mechanism

Different hypotheses about the reaction mechanism of glycerolysis of urea can be found in the literature. Either the preliminary
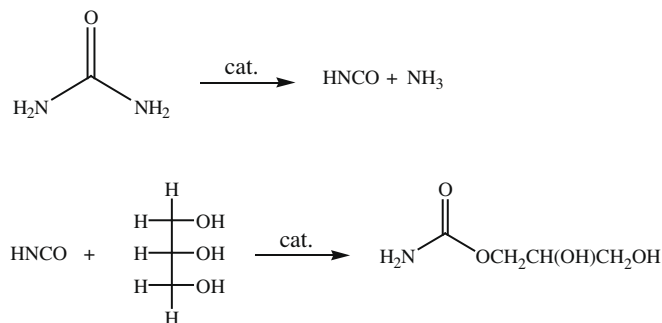
Scheme 4. Proposed mechanism for the glycerolysis of urea using ZnO as catalyst [17].
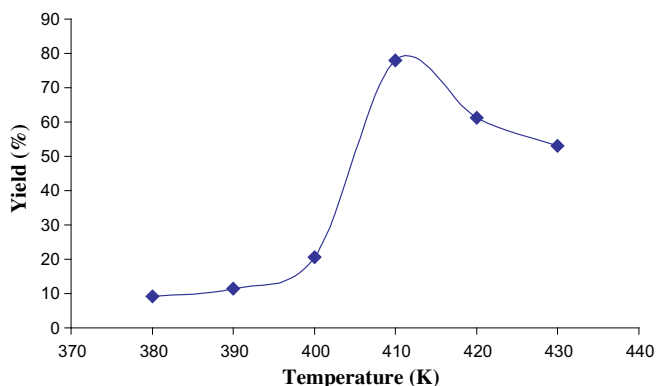
Fig. 8. Trend of formation of glycerol carbonate obtained with respect to the temperature ($P = 20$ Pa, $t = 3$ h).

conversion of urea into iso-cyanic acid [18] or the direct attack by urea to glycerol [26a] has been proposed. We investigated the reactive system trying to gather evidence of the mechanism with the catalyst used in this work.

3.2. Reaction of urea under the reaction conditions used in this work

As reported in the literature [18], using some metal oxides as catalysts in the alcoholysis of urea, an IR peak at about 2220 cm^{-1} (Fig. 1, curves 1 and 2) was noted attributed to the formation of isocyanic acid (O=C=N stretching). According to the authors, the first step of the reaction of urea involves, thus, its activation with loss of a molecule of ammonia to afford isocyanic acid (HNCO); the latter is proposed to react with glycerol and to form the carbamate and then the carbonate (Scheme 4).

The authors proposed that the formation of isocyanic acid is the key step in the reaction because the most active catalysts in the conversion of urea into carbonate afforded the largest amount of isocyanic acid.

Fig. 1 shows that using either titanosilicalite (curve 3) or γ-ZrP (curve 4) no signal was observed around 2220 cm^{-1}, which means that no isocyanic acid was formed during the reaction. In our opinion, with the catalysts which we have used (titanosilicalite and γ-ZrP) a different mechanism must be operating in which urea reacts directly with glycerol with the simultaneous release of ammonia and formation of the carbamate, as we discuss below.
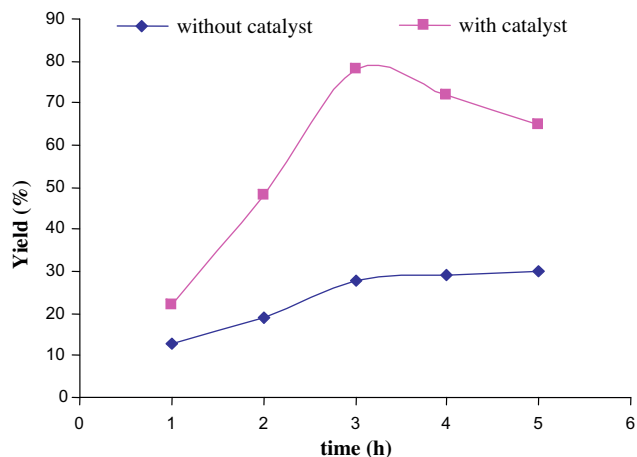

Fig. 9. Trend of yield of glycerol carbonate with the time of reaction.

As a matter of fact, we never detected isocyanic acid in our reaction mixtures. The direct reaction of urea with glycerol improves the yield of carbonate. In fact, isocyanic acid forms very strong intermolecular hydrogen bonds that lead to the formation of dimers and trimers that can very scarcely be avoided [32]. We have shown that an authentic sample of the trimeric isocyanic acid (HNCO)$_3$ very scarcely reacts with glycerol under the reaction condition used in this work. Such side reaction (isocyanic acid formation) apparently subtracts urea to the glycerolysis reaction. It is worth noting that the oligomeric structures of HNCO have IR bands in the same region as the ν_1 fundamental of the monomeric isocyanic acid [32]. It is, thus, also possible that the signals observed using Zn catalysts [18] are due to the oligomeric compounds more than to the monomer.

3.3. The mechanism of formation of the carbonate

The formation of glycerol carbonate **3** takes place, thus, in two consecutive steps, the first of which is the formation of the terminal carbamate species **2** in Scheme 3 – Step A (as confirmed by ^{13}C NMR studies which rule out the attack at C-2 of glycerol, see Section 2) with the removal of the first molecule of ammonia, followed by the formation of carbonate **3** in the second step with the contemporary elimination of the second molecule of ammonia (Scheme 3 – Step B).

Noteworthy, the formation of **3** also takes place *via* a thermal process with a conversion yield of **1** of roughly 28% (Entry 1 in Table 1). Several other studies have shown that Step A of the process occurs at a lower temperature than Step B [26a and references therein] which is accelerated by an opportune catalyst. According to some reports in the literature [18], the most suited catalysts are metal oxides characterized by a specific ratio (0.32–1.22) between the acid and basic sites, but other metal systems are equally active [26a].

We made a wide screening of quite different metal systems characterized by different physical and chemical properties [25] to identify the best systems that might improve the catalytic conversion of **1** and urea into **3**. Particular attention was paid to the recoverability of the catalyst for a possible re-use in subsequent cycles of reaction. Table 1 presents some information on a selected number of the used catalysts: only the most representative of the various classes of compounds are listed.

Catalysts at the Entries 2–7 in Table 1 are practically inactive as the conversion of **1** into **3** observed in their presence is almost the same as observed in a pure thermal process (Entry 1). Titanosilicalite shows a significant activity only when an excess of glycerol is used with respect to urea (Entry 8, Table 1), a condition that we tried to avoid as glycerol is more expensive than urea, our efforts were to keep as much as possible the reactive molar ratio of glycerol–urea close to 1, also if the former was used as solvent and reagent [22,26]. The most active catalysts were those based on γ-ZrP (zirconium phosphate). Such compounds are known since long [24,27–29]. For the synthesis of γ-ZrP we used the synthetic methodology reported in Refs. [22,24]. Crystalline γ-ZrP has a layered structure (Fig. 2) in which the interlayer distance is determined by the phosphate HO-groups and the molecules of water. In the case of the γ-ZrP, the distance between two layers is about 12.25 Å, but it can be reduced to 9.8 Å in the case of β-ZrP [27]. γ-ZrP can be loaded with large organic cations, naked metal ions or metal complexes which occupy interlayer positions and interact via H-bonding with P–O or P–OH groups [30,31].

The resulting materials show interesting catalytic properties in hydrogenation and hydrodechlorination reactions of aromatic systems [30,31]. In this work, we tested either γ-ZrP itself or γ-ZrP loaded with Zn(II)-cations, considered that Zn-compounds were used as catalysts in the patent literature [20].

The conversion yield in the latter case (Entry 11, Table 1) was not better than that exhibited by γ-ZrP alone (Entries 12–14), indicating a scarce involvement of Zn in catalysis or a scarce contribution to reinforce the effect of γ-ZrP itself. As Zn(II) cations are situated between the layers, from these data one can infer that catalysis based on γ-ZrP does not occur in the interlayer space, but at the outside surface of γ-ZrP. We tested other intercalated systems without any better achievements [25]. The size of glycerol and the –OH groups may prevent the migration of molecules of the substrate into the interlayer space so that all the chemistry is done at the external surfaces.

It is worthy to mention that in other catalytic reactions, such as the hydrogenation of benzene, the activity of the catalyst depends on the nature and the amount of intercalated metal system [30,31].

In the presence of γ-ZrP, the glycerolysis reaction proceeded fast enough without solvent, using a molar ratio glycerol/urea close to 1. The conversion of glycerol into glycerol carbonate was over 80% as measured by gas-chromatography. The isolated yield of pure-distilled **3** was 76% [22]. This is the first case in which the formed carbonate has been isolated in a pure form.

Using γ-ZrP as catalyst, a clear liquid phase was obtained at the end of the reaction with the catalyst that was totally separated at the bottom of the reactor so that it was very easily recovered and re-used in a second cycle of reaction showing almost the same performance (Fig. 3). In order to minimize the use of glycerol and maximize the yield of carbonate we started the reaction with a slight excess of glycerol (molar ratio glycerol–urea from 1.2 to 2 [22]) and after the first cycle (the maximum yield of conversion was reached in general after 3 h with a load of 0.6–1% catalyst maximum), we isolated the formed carbonate [22] by extraction and added an equimolar amount of urea/glycerol to the residual mixture. Such cycle was repeated several times. Fig. 3 shows the conversion of glycerol in subsequent cycles of reaction when either the catalyst was kept in the reaction medium to which subsequent portions of urea/glycerol were added or it was recovered at the end of two cycles, calcinated and re-used for two more cycles.

In the first case (lower curve, Fig. 3) the catalyst showed a progressive loss of selectivity from the third cycle onwards, while maintaining the same conversion yield of urea: the lower selectivity was due to the formation of a co-product, which is now under structural characterization, formed upon elimination of water instead of ammonia from **2**. Such product was not formed when the catalyst was recovered after two-three cycles, calcinated and re-used so that the catalyst maintained its efficiency and selectivity (upper curve in Fig. 3).

3.4. Characterization of the catalyst by TPD techniques before and after its use

We carried out a comparative analysis of the catalyst before and after use (three cycles) in catalysis. Key issues were to ascertain whether the γ-ZrP chemisorbed or not the NH_3 released in the reaction and how the modification of the catalyst influenced the selectivity of the reaction. The newly prepared catalyst, after calcination at 773 K, was characterized for its acid and basic properties using the TPD technique.

NH_3 (preferred to pyridine as ammonia is released in the reaction) and CO_2 were used for the determination of acid and basic sites, respectively. The NH_3 chemisorption and the relative TPD on the freshly prepared catalyst without any thermal treatment are shown in Fig. 4 (black curve). The main features of such test were a large amount of ammonia chemisorbed (33.3 mL/g) (Table 2). The profile obtained for the TPD analysis of desorption of NH_3 with programmed temperature (Fig. 4a) showed two peaks: the first had an area equal to 8.49×10^{-2} with a maximum at about 353 K due to medium/low strength acid sites. The second had an

area of 1.97×10^{-2} and a maximum at about 873 K, attributed to high strength acid sites.

Literature data about the assignment of peaks below and around 373 K are somewhat controversial. In some cases [33], authors tend to label only the peaks well above 373 K as due to chemisorbed ammonia, considering peaks below such temperature as due to physisorbed ammonia. In other cases [34], peaks just below 373 K are attributed to desorbed ammonia from weak acid Bronsted sites. In our case, we observed that the first peak changes its position with the nature of the catalyst and with the calcination time for a given catalyst from 360 to 390 K [25]. The high temperature and the large variation of the position push us to attribute such signal to ammonia desorbed from weak acid sites more than to physisorbed ammonia. For the latter a lower desorption temperature would be expected (we found peaks in the range 320–340 K) that should not depend too much on the calcination time of a catalyst.

The same analysis was carried out for the determination of basic sites, using carbon dioxide as probe gas. It was absorbed at 293 K and released with a temperature rise rate of 10 K/min up to 1273 K. Also in this case the catalyst was previously pre-treated at 773 K for 2 h in a nitrogen flow. The carrier gas during TPD was helium. The total CO_2 volume absorbed during the chemisorption was 0.826 mL/g of catalyst corresponding to 0.034 mmol of basic sites per g of catalyst. The TPD curve shows a small peak with a maximum at 363 K with an area equal to 4.32×10^{-2} due to the weak basic sites. A second peak, much less intense, having area equal to 1.07×10^{-2} at 823 K assigned to medium/high strength basic sites and a third very intense peak was located at 1023 K most probably due to the loss of constitution water, more than to desorbed CO_2 (Fig. 4b). These features allow to conclude that the catalyst zirconium phosphate contains both acid and basic sites and their ratio indicates that the behaviour of γ-ZrP prevalently is that of a weak acid catalyst with a ratio acid sites/basic sites equal to 4.1, well above the limit reported to be typical of an active metal oxide catalyst [18].

When the freshly prepared γ-ZrP was calcined for 2 h at 773 K, the uptake and release of NH_3 were quite different. As Fig. 4a (red curve) shows, the amount of NH_3 taken up by weak acid sites is much lower and the total NH_3 uptake is 10% of that of a non calcined sample (compare items 2 and 1 in Table 2): only 0.141 mmol of total acid sites per gram of catalyst (assuming a first order kinetics) was found.

We used the same technique for analyzing the catalyst after use in catalysis. After five cycles, in order to magnify the difference from the starting catalyst, we recovered the γ-ZrP, washed it with methanol and dried at room temperature. Then we carried out a TPD experiment and monitored the ammonia taken up and released from the sample. A first observation is that under the reaction conditions (408 K) NH_3 is not taken up by the catalyst. The desorption curve (Fig. 4a, green curve[1]) of NH_3 taken up at 293 K shows only slight humps at about 343 and 630 K due to the release of ammonia bonded to weak and medium–strong acid sites, respectively. Conversely, a significant peak is found at 823 K due to NH_3 bonded to strong acid sites. The comparison of the TPD curves before and after catalysis on the same sample of γ-ZrP shows an increase of the amount of medium/strong acid sites and a decrease of weak acid sites after use in catalysis. Interestingly, the total ammonia chemisorbed on the recovered catalyst is equal to 4.29 mL/g that must be compared with the amount of the starting calcinated catalyst (3.16 mL/g). There is, thus, an increase of the acidity (mainly due to strong sites) of the catalyst that changes its activity and selectiv-

---

[1] For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

ity towards the formation of glycerol carbonate and causes the formation of the by-product which is now under complete characterization (^{13}C NMR data support a cyclic carbamate structure which can be formed upon elimination of water instead of NH$_3$ from **2**). Therefore, during the glycerolysis of urea, using the catalyst in several subsequent cycles, there is an increase of the acidity of the catalyst, most probably due to the formation of –OH moieties due to adventitious water carried by the reagents (urea and glycerol) not completely anhydrous. In any case, the number of the total acid sites on the catalyst during its use in catalytic runs is higher than that of the starting calcinated catalyst, but still much lower than that characteristic of the freshly prepared catalyst before calcinations, as demonstrated by the quite different volume of absorbed ammonia (4.289 mL/g vs. 33.302 mL/g). (Table 2) On the basis of these data we can conclude that the increase of the strong acid sites on the γ-ZrP modifies the selectivity of the catalyst that promotes the formation of the by-product. As mentioned above, the catalyst does not adsorb NH$_3$ at the reaction temperature (408 K), as it is shown by the amount of NH$_3$ released upon thermal treatment, and, as a consequence, the amount of NH$_3$ taken up by the catalyst is only a very minor percent (0.001%) of the total NH$_3$ formed in the glycerolysis reaction. The ammonia formed in the reaction is, thus, almost quantitatively eliminated from the reactive system using the techniques described above and in detail in [22]. It is worthy to note that the use of the catalysts changes also the chemisorption of CO$_2$, as shown in Fig. 4b. The latter features, also if quite interesting and supporting that during the catalytic cycles the catalyst changes its nature, are less relevant to the specific issue of the uptake by the catalyst of the released gas during the reaction, that is relevant to ammonia but not to CO$_2$.

3.5. Identification of intermediates and products in the reacting mixture

Fig. 5 shows the IR spectrum of the reacting mixture after 1 h during the first cycle: the band at 1786 cm^{-1} due to the formed glycerol carbonate is accompanied by a band at 1712 cm^{-1} due to the carbamate formed in the first step of the reaction of urea with glycerol.

The bands at 1670 and 1620 cm^{-1} are due to the C=O stretching vibration and N–H bending vibration of urea, respectively.

After the fifth cycle (Fig. 6), the signal due to glycerol carbamate (carbonyl at 1712 cm^{-1}) is scarcely evident while a new carbonyl signal (1736 cm^{-1}) also typical of a carbamate carbonyl, but shifted to higher wave numbers, appears. It is attributed to the by-product that, as mentioned above, results to be a cyclic carbamate, as supported by ^{13}C NMR.

The {^{1}H} ^{13}C NMR spectrum of the reaction mixture at the end of the fifth cycle and after extraction of the carbonate (Fig. 7) is quite clean and contains a clear indication of the presence and nature of the by-product. Besides the signals of glycerol (*) and residual (after extraction) glycerol carbonate (#), the spectrum shows a set of three signals at 42, 62 and 77 ppm (ç) due to the by-product observed: they fit well with a cyclic carbamate structure. It is interesting to note that such new compound was formed only after several cycles and did not appear during the first two cycles of reaction nor when the catalyst was isolated after two cycles, calcinated and reused. This confirms that its formation is promoted by the modified catalyst that shows more strong acid sites than the starting calcinated catalyst.

3.6. Influence of the reaction parameters on the conversion yield and selectivity

The temperature and pressure, the reaction time and the presence of a solvent play the key roles in the catalyzed reaction.

Fig. 8 reports the trend of glycerol carbonate formation with respect to the temperature of the reaction. The reaction was carried out at 20 Pa (pumping away the formed NH$_3$) for 3 h. The reaction resulted to be strongly temperature dependent: in fact, up to 400 K the reactivity of the system glycerol–urea remained rather low.

A sudden rise of the curve was observed between 400 K and 415 K, above which a neat decrease of the selectivity towards glycerol carbonate was observed, with increase of formation of the by-product.

Following a similar approach, the dependence on the pressure was investigated. In particular, the reaction was carried out under vacuum or at atmospheric pressure under a continuous stripping of NH$_3$ that was collected [22].

Fig. 9 shows the influence of time of reaction on the conversion of glycerol into carbonate.

After 3 h of thermal reaction, (no catalyst) a formation of 28% of glycerol carbonate was reached that remained almost constant during the following 2 h. Conversely, in the catalyzed process the carbonate yield reached 80% after 3 h. A decrease was observed during the following 2 h due to a loss of selectivity caused by the production of the by-product cited above, still remaining the conversion of urea at the same 80% level.

The catalyst:reagent (glycerol or urea) was kept in the interval 0.6:1.5%, an increase above such level did not significantly improve the rate of conversion of the reagents into the carbonate.

4. Conclusions

The glycerolysis of urea represents an interesting synthetic procedure for glycerol carbonate that may have an industrial application. The good conversion of glycerol (80%), the high selectivity (100% under controlled conditions), the easy separation of the catalyst and its full recovery, the recovery of NH$_3$ and the continuous separation of carbonate make the methodology described by us very promising. The knowledge developed on the influence of the parameter space on the reaction yield and selectivity and the possibility of working under different reaction conditions (batch or continuous flow, low pressure and ambient pressure) make the technology of potential industrial application.

Acknowledgments

References

[1] Y. Zheng, X. Chen, Y. Shen, Chem. Rev. 108 (2008) 5253.
[2] M. Kim, S.O. Salley, K.Y.S. Ng, Energy Fuels 22 (6) (2008) 3594.
[3] M. Czauderna, J. Kowalczyk, J. Chrom. B 858 (2007) 8.
[4] I.G. Farben in Oppau and Hydebreck, 1943.
[5] Z.-X. Wang, J. Zhuge, H. Fang, B.A. Prior, Biotechnol. Adv. 19 (2001) 201.
[6] D. Bondioli, La Chim. e l'Industria (2004) 46. March.
[7] K. Klepáčová, D. Mravec, M. Bajus, Appl. Catal. A: Gen. 294 (2) (2005) 141.
[8] M. Aresta, A. Dibenedetto, in: P. Barbaro, C. Bianchini (Eds.), Catalysts for sustainable energy production, 2009, 444 pp.
[9] C. Gätgens, U. Degner, S. Bringer-Meyer, U. Herrmann, Appl. Microbiol. Biotechnol. 76 (2007) 553.
[10] Cooper, Brian, US Patent 4900668, 1990.
[11] W.C. Ketchie, M. Murayama, R.J. Davis, J. Catal. 250 (2007) 264.
[12] V. Plasman, T. Caulier, N. Boulos, Plast. Addit. Compd. 7 (2) (2005) 30.
[13] D. Randall, R. De Vos, Eu. Pat., EP 419114, 1991 to Imperial Chemical Industries PLC, UK.
[14] M. Weuthen, U. Hees, Ger. Pat., DE 4335947, 1995 to Henkel K.-G.a.A., Germany.
[15] J.J. McKetta (Executive Ed.), W.A. Cunningham (Associate Ed.), Encyclopedia of Chemical Processing and Design, vol. 20, Marcel Decker, New York, 1984, p. 177.
[16] (a) C. Vieville, J.W. Yoo, S. Pelet, Z. Mouloungui, Catal. Lett. 56 (1998) 245;
    (b) Y. Patel, J. George, S.M. Pillai, P. Munshi, Green Chem. 11 (2009) 1056.

[17] (a) M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, J. Mol. Catal. A 257 (2006) 149;
(b) T. Sakakura, K. Kohno, Chem. Commun. (2009) 1312;
[c] J. George, Y. Patel, M. Pillai, P. Munshi, J. Mol. Catal. A: Chem. 304 (2009) 1.
[18] Q. Li, W. Zhang, N. Zhao, W. Wei, Y. Sun, Catal. Today 115 (2006) 111.
[19] M. Okutsu, T. Kitsuki, JP 2007039347, 2007 to Kao Corp., Japan.
[20] C. Sylulli, Z. Muloungui, J.-W. Yoo, A. Gaset, EP 0955298B1, 2001.
[21] (a) M. Okutsu, T. Kitsuki, EP 1156042A1, 2001 to Kao Corp., Japan.;
(b) T. Sasa, M. Okutsu, M. Uno, JP 2008285457 A, 2008 to Jpn. Kokai Tokkyo Koho.
[22] M. Aresta, J.L. Dubois, A. Dibenedetto, F. Nocito, C. Ferragina, EP 08305653.1, 2008 to Arkema, France.
[23] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, England, 1986.
[24] S. Allulli, C. Ferragina, A. La Ginestra, M.A. Massicci, N. Tomassini, J. Inorg. Nucl. Chem. 39 (1977) 1048.
[25] F. Nocito, Ph.D. Thesis, Department of Chemistry, University of Bari, 2009.

[26] (a) M. Aresta, A. Dibenedetto, C. Devita, O.A. Bourova, O.N. Chupakhin, studies on surface sciences and catalysis (carbon dioxide utilization for global sustainability) 153 (2004) 213.;
(b) P. Albano, M. Aresta, M. Manassero, Inorg. Chem 19 (1980) 1069.
[27] A. Clearfield, R.H. Blessing, J.A. Stynes, J. Inorg. Nucl. Chem. 30 (1968) 2249.
[28] S. Yamanaka, M. Tanaka, J. Inorg. Nucl. Chem. 41 (1979) 45.
[29] A. Christensen, E.K. Andersen, I.G.K. Andersen, G. Alberti, N. Nielsen, M.S. Lehmann, Acta Chem. Scand. 44 (1990) 865.
[30] P. Giannoccaro, M. Gargano, A. Fanizzi, C. Ferragina, A. Leoci, M. Aresta, J. Mol. Catal. 227 (2005) 33.
[31] P. Giannoccaro, M. Gargano, A. Fanizzi, C. Ferragina, M. Aresta, Appl. Catal. 284 (2005) 73.
[32] J.A. Teles, G. Maier, B.A. Hess, L.J. Schaad, M. Winnewisser, B.P. Winnewisser, Chem. Ber. 122 (1989) 753.
[33] M. Niwa, M. Iwamoto, K-i. Segawa, Bull. Chem. Soc. Jpn. 59 (1986) 3735.
[34] H. Kosslick, H. Landmesser, R. Fricke, J. Chem. Soc., Faraday Trans. 93 (1997) 1849.