AN INTEGRATED APPROACH TO THE SYNTHESIS OF ORGANIC CARBONATES: DISCOVERY OF NEW CATALYSTS

Michele Aresta, Angela Dibenedetto and Carlo Pastore

Department of Chemistry, University of Bari
Campus Universitario – 70126 Bari - Italy

Introduction

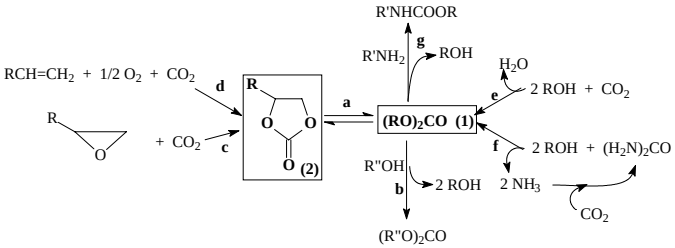
Molecular organic carbonates are versatile compounds used as solvents or reagents in the chemical industry, or as additives to fuels.[1] The latter application and their use as monomers for polymers may expand in the near future, causing a large increase of their demand on the world market. As the current synthetic technology is represented by the use of phosgene (that is banned in several countries) as building block, the development of new synthetic methodologies for organic carbonates is receiving much attention worldwide. The replacement of such toxic raw material with carbon dioxide seems to be very attractive and interesting. In fact, it responds to the "green chemistry" principles by using clean and safe technologies, also implementing the atom-economy strategy. Moreover, the utilization of carbon dioxide represents a way of carbon-recycling, saving natural resources.

In this paper we describe a pool of CO_2-based "convergent synthetic technologies" such as the direct oxidative carboxylation of olefins, the carboxylation of epoxides, the direct carboxylation of alcohols, the alcoholysis of urea coupled with the trans-esterification reaction for the synthesis of organic carbonates, either linear or cyclic. The reactivity of Group 5 (V, Nb, Ta) element compounds, used as catalysts in these reactions, will be discussed and a comparison of their reactivity will be made.

Our goal, besides demonstrating the effectiveness and the benefits of networking such reactions, is the identification of a metal that may provide selective catalysts per each of the routes **a**-**g** in Scheme 1 or better, the development of a many-purpose catalyst that may drive several reactions.

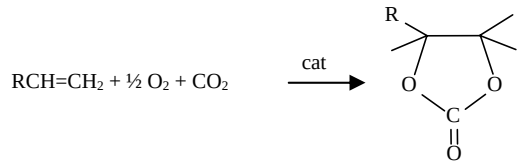
Results and Discussion

Scheme 1 represents the pool of convergent synthetic methodologies for the preparation of either linear **(1)** or cyclic **(2)** carbonates, and the **(1) = (2)** inter-conversion, through the trans-esterification reaction. All synthetic routes respond to the "green chemistry principles" and use safe reagents and operative conditions.



Scheme 1. Convergent methodologies for the synthesis of linear (**1**) and cyclic (**2**) carbonates

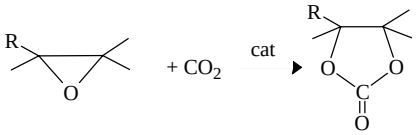
Since long, our research group is involved in the use of Nb-compounds as catalysts for the synthesis of organic cyclic carbonates. We have reported[2] that Nb_2O_5 is an active catalyst in the direct oxidative carboxylation of olefins (Eq. 1) and extensively discussed the role of the temperature and solvent on the conversion yield and selectivity.



(1)

We have shown that dimethylformamide (DMF) or dimethylacetamide (DMA) are good solvents for such reaction and that heterogeneous catalysts have a longer life-time than homogeneous ones[3] under the same operative conditions. The oxidative carboxy lation of olefins can be split into two reactions, namely the epoxidation of olefins using dioxygen, that is a quite interesting process *per se*, and the carboxylation of the resulting epoxides. The reaction conditions strongly influence the yield and selectivity of the whole process. The nature of the solvent plays a key role in the carboxylation of epoxides, a reaction that is promoted by amides[4] like DMF or DMA that alone are able to carboxylate the epoxides. Conversely, in solvents like aromatics and ethers the reaction does not occur or takes place at a limited extent also in presence of heterogeneous metal systems under the same operative conditions. These findings justify the use of DMF as solvent in the oxidative carboxylation of olefins. The importance of such synthetic approaches (routes **c** and **d** in Scheme 1) results much better if one considers that their coupling to the trans-esterification reaction (route **a** in Scheme 1) may make the oxidative carboxylation of olefins or the carboxylation of epoxides a new approach for the synthesis of both linear and cyclic carbonates.

We have clearly demonstrated the efficacy of Nb(V) and Nb(IV) compounds as catalysts for the conversion of epoxides into the relevant carbonates (Eq. 2) with a selectivity >99%. Also, we have



(2)

shown that Nb(V)-oxide is an active catalyst for the carboxylation of pure enantiomers of chiral epoxides with total retention of the configuration.[5] Additionally, Nb(IV) complexes with optically active ligands promote the carboxylation of racemic mixtures of styrene- or propene-oxide with an interesting enantiomeric excess.[5]

Interestingly, we have found that Nb(V) compounds are also active catalysts for the trans-esterification reaction (TER). We have used either $Nb(OR)_5$ compounds or Nb(V)-oxide[6] with interesting conversion yields and 100% selectivity (see below).

Besides such reactions, we have investigated new routes to linear carbonates,[7a] such as the direct carboxylation of alcohols[8] (Eq. 3, or route **e** in Scheme 1) and the reaction of urea with alcohols[9] (Eq. 4 or route **f** in Scheme 1). Also in this case Nb(V) compounds are good catalysts. In particular, $Nb(OR)_5$ (R=Me, Et, allyl) show an interesting activity for the carboxylation of alcohols[8] (Eq. 3), and Nb_2O_5 is active in the alcoholysis of urea[9] (Eq. 4).

$$2\ ROH + CO_2 \longrightarrow (RO)_2CO + H_2O \qquad (3)$$

$$2\ ROH + (H_2N)_2CO \longrightarrow RO)_2CO + 2\ NH_3 \qquad (4)$$

In the carboxylation of alcohols, $Nb(OR)_4(OCOOR)$, generated in the reaction of $Nb(OR)_5$ with CO_2, is the active catalytic species. Although such reaction suffers of thermodynamic limitations, the catalyst can be recovered and used several times as shown in Figure 1, improving the total turnover number.

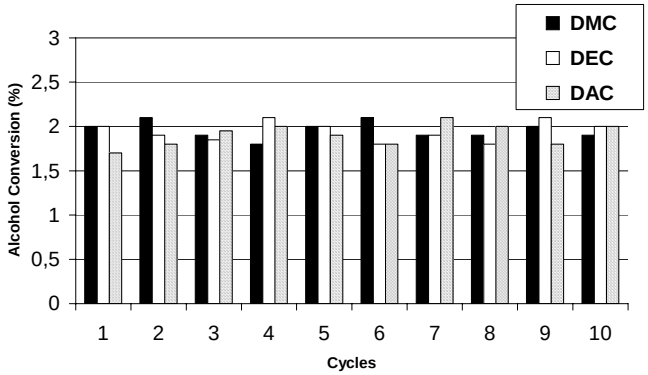


Figure 1. Stability of the $Nb(OR)_5$ catalysts (R= Me, Et, allyl) over ten runs in the carboxylation of the relevant alcohols.

Besides such reaction, $Nb(OR)_5$ has been shown to play a catalytic role also in the trans-esterification reaction (TER) that promotes the inter-conversion of carbonates, as depicted in Scheme 1, route **a**. Conversely, Nb_2O_5 that promotes the carboxylation of epoxides and the oxidative carboxylation of olefins, is also an active catalyst for the alcoholysis of urea and the TER. However, it is possible to utilize a class of catalysts derived from a single element for the synthesis of a wide range of linear and cyclic carbonates by using a sequence of reactions not based on the use of phosgene.

For the trans-esterification reaction, we have also tested several compounds of V and Ta in the oxidation state five, and compared their efficiency to the Nb-systems and to other catalysts (TiO_2) reported in the literature. In such reactions, we have used three classes of compounds, namely pentalkoxo- [$M(OR)_5$, M = Nb or Ta] and oxo-trialkoxo-metal complexes [$MO(OR)_3$, M = Nb, V] (Fig. 2), or metal-oxides [Nb_2O_5, Nb_2O_4, Nb_2O_3, NbO, V_2O_5, V_2O_4, V_2O_3] (Fig. 3).

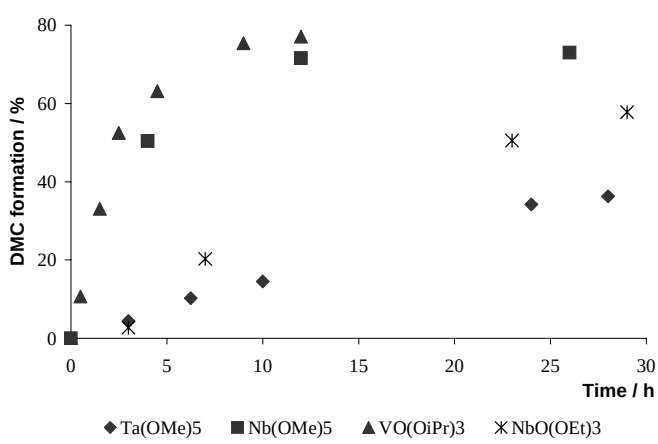


Figure 2. Activity of several Group 5 element alkoxides- or oxo-alkoxides as transesterification (EC→ DMC) catalysts

Ethylene carbonate (EC) was selected as the cyclic carbonate, due to the fact that it can be effectively synthesized from the relevant epoxide and CO_2 using several catalysts, including Nb_2O_5 under heterogeneous conditions, or Nb(IV)- and Nb(V)-complexes as homogeneous catalysts.

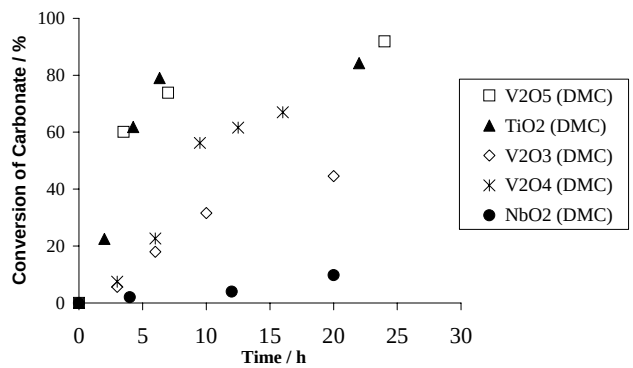


Figure 3: Activity of Group 5 metal oxides as trans-esterification catalysts.

Satisfactory results have been obtained using several of the Group 5 element catalysts in the trans-esterification of ethylene carbonate with MeOH, EtOH or allyl-OH, as shown in Figg. 2 and 3.

In particular, V_2O_5 has shown a higher efficiency, over the long reaction time, than TiO_2 that is used in industrial applications. (Fig. 3)

Conclusions

The network of reactions represented in Scheme 1 has been shown to be fully operative. Using Group 5 element compounds as catalysts it has been possible to develop new synthetic approaches to both linear and cyclic carbonates. The same compounds are good trans-esterification catalysts. Therefore, Group 5 element derivatives represent a class of compounds with a multipurpose application in catalytic processes relevant to CO_2 utilization.

Acknowledgments. We gratefully acknowledge the financial support by MIUR Project 2003039774 and the experimental assistance provided by Ms Olga Burova and Cira Devita.

References

(1) Carbon Dioxide Recovery and Utilization, Aresta, M. Ed., Kluwer Academic Publishers, London **2003**.
(2) Aresta, M.; Dibenedetto, A. *J. Mol. Catal. A: Chemical* **2002**, *182-183*, 399.
(3) Aresta, M.; Dibenedetto, A.; Tommasi, I. *Eur. J. Inorg. Chem.* **2001,** 1801-1806.
(4) Aresta, M.; Dibenedetto, A.; Gianfrate, L.; Pastore C. *J. Mol. Catal. A: Chemical*, **2003**. *204-205*, 245
(5) Aresta, M.; Dibenedetto, A.; Gianfrate, L.; Pastore C. *Appl. Catal.* **2003**. in press.
(6) Aresta, M.; Dibenedetto, A.; Pastore, C. *Studies in Surface Science and Catalysis*, **2003**, in press.
(7) Aresta, M.; Dibenedetto, A.;. Pastore, C. *XXI Congresso Nazionale della Società Chimica Italiana*, Torino, June 22-27, **2003**, IN CO 031; b) Choi, J.C.; Sakakura, T.; Sako, T. *J. Am. Chem. Soc.* **1999**, *121*, 3793; c) Ballivet-Tkatchenko, D.; Douteau, O.; Stutzmann, S. *Organometallics* **2000**, *19*, 4563.
(8) Aresta, M.; Dibenedetto, A.; Pastore, C. *Inorg. Chem.*, **2003**, *42*, 10, 3256.
(9) Aresta, M.; Dibenedetto, A.; Devita, C.; Bourova, O.; Chapukin, O.N. *Studies in Surface Science and Catalysis*, **2003**, in press.