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HETEROGENEOUS CATALYSIS IN SUPERCRITICAL CO₂ CONDITIONS APPLICATION IN DIMETHYL CARBONATE SYNTHESIS

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Abstract. In the present work, the development of a new catalytic system based on the synthesis of dimethyl carbonate (DMC) starting from methanol and carbon dioxide in supercritical conditions was investigated. Various metallophthalocyanines (MPc: ZnPc, CoPc, AlClPc, CuPc(SO₃Na)₄, CoPc(SO₃H)₂₋₃, ZnPc(SO₃H)₂₋₃) were used as catalysts. In a first step reactions were carried out in homogeneous phase. No reaction was observed with non substituted phthalocyanines. In the case of Co and Zn substituted by SO₃H moieties a DMC formation was observed. Tests are carried out in a 95 mL autoclave; the organics were separated from the catalyst via a vacuum distillation with a liquid nitrogen trap. The reaction products are analyzed by a GC-FID and GC-MS.

Key-words. dimethyl carbonate, cyclic carbonate, supercritical carbon dioxide

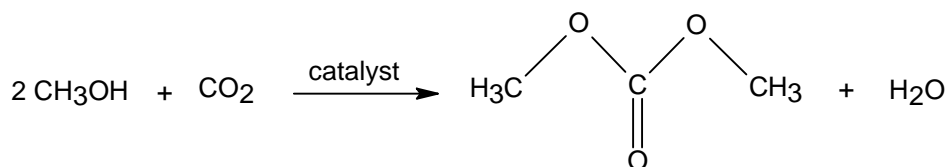
INTRODUCTION

From the appearance of the concept of "green chemistry" in 1990 and the emergence of twelve recommendations that now govern the research in the field of chemical industry, the work on the synthesis of green molecules have turned to new high performance techniques that avoid the use of hazardous products. In the specific case of dimethyl carbonate, the global production is about 100 Kt/year[1] but could easily reach 1Mt/year, if its full potential was exploited. Indeed, currently, the DMC, a non-toxic, non-carcinogenic, non-mutagenic reagent, has a great environmental interest. For example it is used as source of polycarbonates [2, 3]. In the EniChem process for the synthesis of aromatic polycarbonates, the use of the DMC and diphenylcarbonate (DPC) as intermediates avoids, not only the use of phosgene, but also the use of methylene chloride as a solvent, and prevents the formation of NaCl as a co-product. DMC is also employed in alkylation and methoxycarbonylation reactions in the pharmaceutical industry [4]. For example, the mono-C-methylation of aryl derivatives, conducted in DMC, gives higher conversion rate and selectivity, respectively 90% and 99%, to produce anti-inflammatory precursors as naproxen, ketoprofen and ibuprofen [5, 6]. It replaces in this case, very toxic compounds such as phosgene, dimethyl sulphate and alkyl halides. As oxidizer, it reacts with cyclic aliphatic ketones to form unsaturated diesters, intermediates in the production of polyesters and polyamides [7]. It has also solvent utilizations. Dimethyl carbonate is an alternative to the use of solvents such as acetone and other carbonyl compounds.

The limitation of the production of DMC is due to the existing synthesis technologies, which are extremely dangerous: the use of phosgene, as for the SNPE process, the mixture of carbon monoxide and oxygen, as for the EniChem process [8], nitric oxide and carbon monoxide, as for the UBE process [9].

To bring it into line with the demands of the green chemistry, research has been carried out to find a cleaner way of synthesis that could be also applied on an industrial scale. Other important environmental problem is the increasing quantity of carbon dioxide, one of the Green House gases, in the atmosphere. Various studies have shown that an utilization of carbon dioxide in the chemical industry together with its storage will help in decreasing the danger concerning the global heating. The reaction between methanol and the CO₂ molecule in the DMC synthesis showed a great interest in chemistry since the only by-product is water (equation 1). One of the most studied series of catalysts is the tin complexes [10, 11, 12, 13] but the main problem is the water contamination of the catalyst which annihilates its activity. Although the acid-base properties of ZrO₂ catalysts [14] are of big interest in the reaction mechanism and no poisoning effect by

water, there is still the low yield inconvenient. Another example is the nickel acetates/ methyl iodide system. Although a base co-catalyst is used the yields are low and the reaction generates HI.



Research has been developed in order to determine the methoxycarboxylation mechanism and to eliminate the thermodynamic constraint and so increasing the yield in DMC. Since carbon dioxide is hardly reactive an efficient catalytic system must be found to activate the CO_2 molecule and make it react with methyl and methoxy moieties. Our work is based on the research of a new heterogeneous catalytic system for the methoxycarboxylation process. The proposed catalyst is a transition metal phthalocyanine. These compounds are considered as non-dangerous [15] and present a high stability towards acids, bases and temperature. The Metal-Nitrogen bond is strong [16] preventing the loss of metal ions in solution, and hence the risk of pollution by heavy metals.

MPcs find interesting properties as the tunable solubility by changing the R moiety with groups like: H, SO_2Cl , X, OH, OCH₃, CN, NO₂, SO_3Na ... Along with the solubility there is also a tunable reactivity depending on the metal center: Al, Fe, Mn, Co, Ni, Cu, Zn. Figure 1 shows the configuration of the metallophthalocyanine molecule.

MPcs have found many applications, such as dyes [17] in paints, inks, textiles, photosensitizers in cancer treatment [18], bleaching agents for detergents [19, 20], desulphurization catalysts for petroleum products and oxidation catalysts for organic pollutants.

As part of the synthesis of organic carbonates, there are several examples of catalytic systems based on metallophthalocyanines. Thus, copper [21] and aluminum [22] phthalocyanines catalyze the formation of cyclic carbonates from propylene oxide and carbon dioxide. Reaction rates are high but with certain metal centers the reactivity increases if a co-catalyst (ionic liquid, tertiary amine) is added. In addition, there is evidence that metallophthalocyanines and similar complexes activate carbon dioxide and make it react with different substrates [23, 24, 25].

The aim of our study is to perform the applicability of this catalyst in the reaction between methanol and carbon dioxide under supercritical conditions. Supercritical fluids exhibit a tunable density by controlling its temperature and pressure. In our case the utilization of supercritical conditions is motivated by the low solubility of metallophthalocyanines in methanol. It is thought that by searching appropriate conditions (temperature and pressure) to get the reaction system in a monophasic state the catalyst solubility will increase significantly.

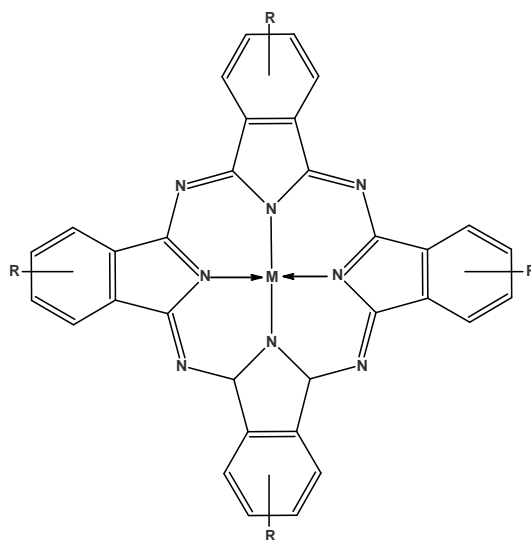


Figure 1. Metallophthalocyanine

EXPERIMENTAL

Materials

All chemicals used were of reagent grade. AlClPc , ZnPc , $\text{CuPc}(\text{SO}_3\text{Na})_4$ were delivered by Acros Organics and CoPc by... $\text{CoPc}(\text{SO}_3\text{H})_{2-3}$, $\text{ZnPc}(\text{SO}_3\text{H})_{2-3}$ were kindly supplied by Europhthal. Methanol and carbon dioxide were delivered from Panreac and Linde respectively.

Tests were carried out in a TopIndustry high pressure autoclave with an inner volume of 95 mL and a magnetically stirrer, 1600 rpm. The maximum temperature and pressure were of 250°C and 340 bar respectively. The reactor was electrically heated and equipped with a Temperature Security High to control the reaction temperature. An ISCO pump was used to control the carbon dioxide volume that was injected in the reactor. The high pressure system layout and photography are shown in figure 2 and figure 3 respectively.

The separation of the catalyst from the organic products was realized with a vacuum distillation vessel using a liquid nitrogen double trap.

Analyses were realized by GC using a capillary column Restek 502.2 (30 m, Ø 0.25 mm, 1.4 µ film) on a Trace GC Ultra gas chromatography supplied by Thermo Scientific. Indeed, a flame ionization detector and a TriPlus autosampler were used.

Preliminary high pressure tests

First tests were carried out in homogeneous. Calculations have been made in order to choose reagents amounts and to establish reaction conditions (temperature and pressure). This preliminary procedure is of great importance because realizing a monophasic reaction system increases the contact between the reagents and the possibility of getting great conversion.

Typical procedure: 20 mL (500 mmol) of methanol and 8.8 mg (0.01 mmol) of catalyst were charged into the autoclave.

Then the reactor was heated up to 140°C. The ISCO pump was charged in liquid CO₂ followed by a compression to the desired pressure (220 bar). Whereafter, carbon dioxide was injected into the autoclave. After 7 hours the system was cooled down and depressurized with the sampler extractor. Then the reactor was opened to recuperate the reaction products. The organics were separated from the catalyst by vacuum distillation and then submitted to a GC analysis.

RESULTS AND DISCUSSION

A first observation is that the solubility of all metallophthalocyanines employed in preliminary tests varies as follows: ZnPc, CoPc, AlClPc, CuPc(SO₃Na)₄ << CoPc(SO₃H)₂₋₃, ZnPc(SO₃H)₂₋₃. The H and SO₃Na substituted phthalocyanines remain in suspension in the presence of methanol while the SO₃H moiety gets the Co and Zn amount totally soluble in CH₃OH. This demonstrates that the aromatic ring substitute plays an important role in phthalocyanine solubility. The enhancement of solubility means a better contact between the reagents and this is also a reason for using supercritical fluid properties.

In previous papers metallophthalocyanines showed good activity in the cyclic carbonates synthesis. An enhancement of the activity is brought by the addition of a base co-catalyst like a tertiary amine or an ionic liquid. In this work it is thought that the reaction mechanism passes through the same steps: the coordination of OCH₃ moiety on the metallic center of the catalyst, then the activation of CO₂ and its insertion in the metal-OCH₃ bond. The last step of the mechanism will be the breaking of CH₃-O bond and the formation of DMC molecule. In addition, breaking of methyl-oxygen bond is more easily realized in the presence of a base co-catalyst. In this study is analyzed the activity of proposed catalysts without co-catalyst.

After separation of organic species a GC-FID followed. Results and some chromatograms are

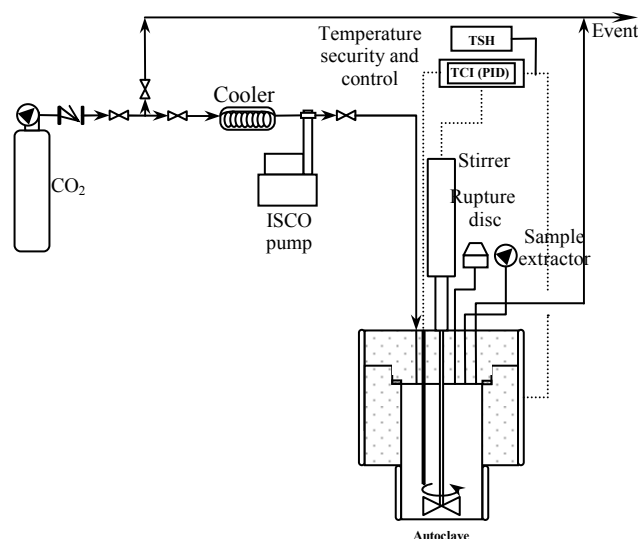


Figure 2. High pressure system for DMC synthesis

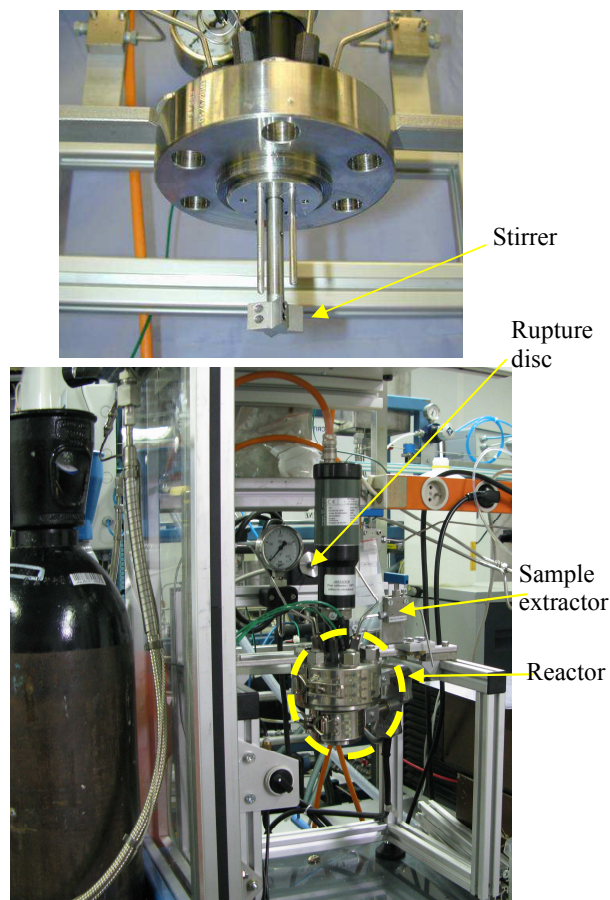


Figure 3. Photography of magnetic stirrer (up) and high pressure system for DMC synthesis (bottom)

shown in the table 1 and figures 4 respectively.

From the first results we can easily observe that the metallophthalocyanines non-substituted or having SO_3Na moieties doesn't catalyze the reaction; the chromatography results show no reaction product than methanol. By the way the two Co and Zn metallophthalocyanines substituted by SO_3H moieties show a certain activity, so that we can see that the turnover frequency number is of 160 and 96 h^{-1} respectively. We may say that we can get an activation of the reaction only with soluble catalysts. The yields are not very high but the reaction seems to be catalytic since the molar ratio of DMC versus the catalyst is 50/1 in the case of $\text{CoPc}(\text{SO}_3\text{H})_{2-3}$.

The chromatogram of organic products issued from the test where $\text{CoPc}(\text{SO}_3\text{H})_{2-3}$ was used is displayed in the figure 4. We can see that there are many signals in this chromatogram but only two of them are reaction products. A comparison of DMC, methanol and test chromatogram shows that the signal at 2.98 min represents a residue from dimethyl carbonate. The signal at 3.23 min is an acetonitrile impurity coming from the methanol as well as the 5.35 min signal. The signal that appears at 6.27 min represents the dimethyl carbonate molecule. Another important signal is at 3.92 min and it is surely a by-product of the reaction. The determination of this secondary product is of great importance in increasing the dimethyl carbonate yield. Furthermore, with this information reaction conditions and amounts of reagents can be changed to get reaction selective. For bringing information about this second organic product a GC-MS analysis is in progress.

Once the second product is determined, a mechanistic study will help for the understanding the reaction. We don't know yet if either the presence of the dimeric form of the phthalocyanines decreases the catalyst activity or the difficulty of reaching the last step of the reaction (breaking the $\text{O}-\text{CH}_3$ bond in methanol to generate a CH_3 moiety).

Catalyst	TOF (h^{-1})
$\text{Cu}(\text{SO}_3\text{Na})_4$	No reaction
AlClPc	No reaction
ZnPc	No reaction
CoPc	No reaction
$\text{ZnPc}(\text{SO}_3\text{H})_{2-3}$	96
$\text{CoPc}(\text{SO}_3\text{H})_{2-3}$	160

Table 1. The formation rates of dimethyl carbonate from CH_3OH and CO_2 with various metallophthalocyanine complexes (reaction conditions: 220 bar, 140°C , 7h, 500mmol CH_3OH , 0.01mmol catalyst and 300mmol CO_2)

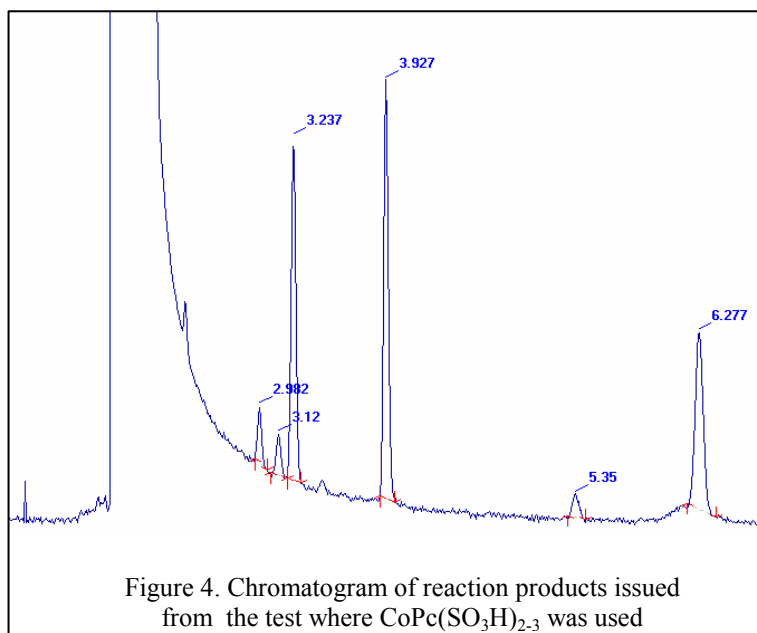


Figure 4. Chromatogram of reaction products issued from the test where $\text{CoPc}(\text{SO}_3\text{H})_{2-3}$ was used

CONCLUSIONS AND PERSPECTIVES

In this work, catalytic activity of $\text{ZnPc}(\text{SO}_3\text{H})_{2-3}$ and $\text{CoPc}(\text{SO}_3\text{H})_{2-3}$ towards the dimethyl carbonate formation from methanol and supercritical carbon dioxide has been evidenced. Other metallophthalocyanines, less soluble in methanol like ZnPc, CoPc, AlClPc, $\text{CuPc}(\text{SO}_3\text{Na})_4$ show no activity in the proposed reaction conditions. Along with the dimethyl carbonate, another secondary product has been found but its identification by GC-MS analysis is in progress. Even the yield is low the reaction is catalytic and a mechanistic study must be undertaken. Furthermore, the modulation of the reaction conditions along with the addition of a base co-catalyst can achieve a greater conversion of methanol.

REFERENCES

- [1] M. Aresta, A. Dibenedetto, Ed. M. Aresta, 2003, 211-260
- [2] D. Delledonne, F. Rivetti, U. Romano, *Applied Catalysis A: General* 221 (2001) 241-251
- [3] F. Rivetti, *Comptes rendus de l'Académie des Sciences. Série IIc, chimie*, 3(6) (2000) 497-503
- [4] P. Tundo, *Pure Appl. Chem.*, 73 (2001) 1117-1124
- [5] M. Selva, C.A. Marques, P. Tundo, *J. Chem. Soc., Perkin Trans.*, 1 (1994) 1041
- [6] P. Loosen, P. Tundo, M. Selva, U.S. Patent, 5278533, 1994
- [7] P. Tundo, S. Memoli, M. Selva, European Patent pending PCT/EP01/09241
- [8] U. Romano, F. Rivetti, N. Di Muzio, US Patent 4,318,862, 1979 by Enichem
- [9] K. Nisihira, K. Mizutare; S. Tanaka, EP Patent Applied for 425, 197 by UBE Industries
- [10] D. Ballivet-Tkatchenko, S. Chambrey, R. Keiski, *Catalysis Today* 115 (2006) 80-87
- [11] T. Sakakura, J.-C. Choi, Y. Saito, T. Sako, *Polyhedron* 19 (2000) 573-576
- [12] D. Ballivet-Tkatchenko, T. Jerphagnon, *Applied Catalysis A: General* 255 (2003) 93-99
- [13] D. Ballivet-Tkatchenko, R. Burgat, S. Chambrey, *Journal of Organometallic Chemistry* 691 (2006) 1498-1504
- [14] K. Taek Jung, A.T. Bell, *Journal of Catalysis* 204 (2001) 339-347
- [15] Japan Chemical Industry Ecology-Toxicity & Information Centre, JETOC information sheet: special issue N° 18 Tokyo: JETOC. (1995)
- [16] A. Ahmad, R.A. Collins, *J. Phys. D : Appl. Phys.*, 24 (1991) 1894-1897
- [17] U. Tsutomu, M. Toshiyuki, M. Yutaka, K. Masaaki, K. Tetsuzo, European Patent 1 832 633 A1 (2007) to Fujifilm Corporation
- [18] G. Holzle, M. Miotto, G. Reinert, R. Polony, US Patent 4497741 (1985) to CIBA GEIGY CORP
- [19] A. Rabion, F. Fajula, J.-R. Bernard, V. Hulea, US Patent WO//2001/048119 to Elf Antar France
- [20] F. Lecomte, S. Drozoz, P. Briot, R. Cadours, European Patent CA2614087 (2006) to Institut Français du Pétrole
- [21] R. Srivastava, T.H. Bennur, D. Srinivas, *Journal of Molecular Catalysis A: Chemical* 226 (2005) 199-205
- [22] D. Ji, X. Lu, R. He, *Applied Catalysis A: General* 2003 (2000) 329-333
- [23] Stephan Schenk, Johannes Notni, Uwe Köhn, Kurt Wermann and Ernst Anders, *Dalton Trans.* (2006) 4191-4206
- [24] Suojiang Zhang, Yuhuan Chen Wenbin Dai, Xingmei Lu, Fuwei Li Ryohei Mori, *Catalysis Today* 115 (2006) 61-69
- [25] J. Costamagna, G. Ferraudi, J. Canales, J. Vargas, *Coordination Chemistry Reviews* 148 (1996) 221-248