Methyl Esters as Efficient and Green Water Suppressors in the Synthesis of Dimethyl Carbonate from CO_2.

Aryane A. Marciniak (PG),[1] Claudio J. A. Mota (PQ)[1,2,3*]

[1] *Universidade Federal do Rio de Janeiro, Escola de Química, CT Bl E, 21941-909, Rio de Janeiro, Brasil.*
[2] *Universidade Federal do Rio de Janeiro, Instituto de Química, CT Bl A, 21941-909, Rio de Janeiro, Brasil.*
[3] *INCT Energia e Ambiente, UFRJ, 21941-909, Rio de Janeiro, Brasil.*

Palavras Chave: *Química verde, dimetil carbonato, CO_2, éster metílico, cinética, catálise.*

Abstract

Methyl esters can be used as efficient and sustainable water suppressor in the reaction of CO_2 with methanol to synthesize dimethyl carbonate (DMC). The carboxylic acids formed could be separated from the medium and recycled into the correspondent methyl esters for further use.

Introdução

Dimethyl carbonate (DMC) has attracted much attention as a nontoxic and biodegradable reagent. The direct synthesis of DMC from CO_2 and methanol (Scheme 1) has strong thermodynamic limitations.[1] Several reagents, such as nitriles, diimides, acetals, oxiranes, among others, have been used as water suppressors, in the synthesis of DMC, to shift the equilibrium. However, many secondary products are formed as wastes, making the whole process not enough sustainable to be used in large scale.

Scheme 1. Direct carbonation of methanol to produce DMC.

We report here the use of methyl esters, with appropriated reactivity toward hydrolysis, as efficient and sustainable water suppressors in the synthesis of DMC from CO_2 and methanol.

Resultados e Discussão

The reactions were carried out in a 100 mL Parr® batch reactor at 48 bar of initial CO_2 pressure, 170 °C and 6 h of reaction time. Bu_2SnO was used as reference catalyst and the molar ratio of the esters (methyl trifluoroacetate and methyl trichloroacetate) to methanol was varied (0.1, 0.25, 0.5, 1.0 and 3.0). The product was analyzed by gas chromatography (Agilent 6850) equipped with a flame ionization detector and HP-PONA capillary column (50 m x 200 µm x 0,50 µm) and the yield of DMC, expressed in terms of mols per mol of the catalyst was calculated using a standard calibration curve.
Figure 1 shows the yields, expressed in turnover number (TON) as mol of DMC formed per mol of catalyst used, as a function of the amount and type of ester suppressor. Both esters tested presented increased DMC yield compared with the reaction without any suppressor. The best results were observed with methyl trichloroacetate, which showed TON of 21.5, when a molar ratio to methanol of 1:1 was used. This result is somewhat surprising because CF_3 is a stronger electron withdraw-ing group than CCl_3. One possible explanation is that the tin catalyst may be involved in the hydrolysis of the esters, coordinating with the carbonyl group. Thus, the methyl trichlroacetate would coordinate better with the tin catalyst, as it has a stronger basicity.

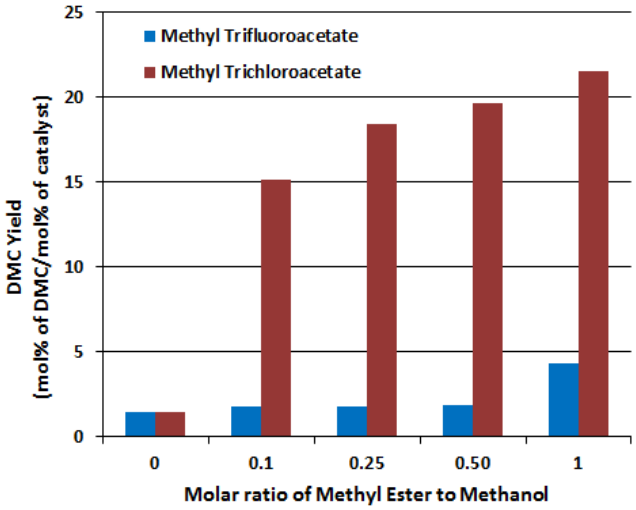

Figure 1. Effect of the methyl ester to methanol molar ratio on the DMC yield. Reaction conditions: 100 mg of catalyst, 73 mmol methanol, 170 °C, 48 bar and 6h.

Conclusões

Methyl esters bearing an electron withdrawing group, such as CF_3 and CCl_3, can be efficient and recycling water suppressors in the synthesis of DMC from methanol and CO_2.

Agradecimentos

FAPERJ and CNPq

[1] Eta, V.; Ma¨ki-Arvela, P.; Leino, A. R.; Kordas, K.; Salmi, T.; Murzin, D. Y.; Mikkol, J. P. *Ind. Eng. Chem. Res.* **2010**, 49, 9609-9617.