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# **Reaction mechanism of dimethyl carbonate synthesis**

## through isotopic labeling experiments

Cécile Daniel, David Farrusseng, Yves Schuurman\*

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON UMR 5256, F-69626 Villeurbanne

\* corresponding author: <a href="mailto:yves.schuurman@ircelyon.univ-lyon1.fr">yves.schuurman@ircelyon.univ-lyon1.fr</a>

#### Abstract

The synthesis of dimethyl carbonate (DMC) from carbon dioxide and methanol was studied over ceria zirconia oxide. When using oxygen-18 labeled ceria zirconia oxide, no oxygen-18 labeled DMC or water was observed. On the other hand, using oxygen-18 labeled methanol led almost exclusively to the formation of double labeled DMC, CH<sub>3</sub><sup>18</sup>O (C<sup>16</sup>O) <sup>18</sup>OCH<sub>3</sub>. These results are used to further elaborate the proposed reaction mechanisms for DMC synthesis. The rate controlling step is identified as a nucleophilic attack of gas phase methanol on surface monomethyl carbonate species to form DMC.

Keywords: oxygen-18; methanol; carbon dioxide; ceria-zirconia; reaction mechanism

#### Introduction

Dimethyl carbonate (DMC) is an attractive product because of its low toxicity and fast biodegradability. It is an important synthon for the production of polycarbonates and a methylating agent, but it can also be used as an additive in gasoline, as a solvent in lithium-ion batteries, or as a substitute for VOCs in paints [1,2]. These large-scale applications are bound to increase the global demand for DMC significantly in coming years.

DMC was formerly produced on an industrial scale by phosgenation, then more recently by oxidative carbonylation of methanol (Enichem process) or by carbonylation of methyl nitrites (UBE process) [1,2]. These synthesis routes are polluting and toxic. The carboxylation of methanol into DMC appears as a green and sustainable alternative and is produced according to the following equation:

$$CO_2 + 2 HO - CH_3 \implies H_3C \longrightarrow CH_3 + H_2O$$

However, the thermodynamic equilibrium of this reaction is strongly shifted to the side of the reactants: the conversion of methanol at equilibrium is less than 1% at reaction temperature. But the selective withdrawal of the produced water allows to reach conversions close to 40%. This can be achieved by adding dehydrating reagents to the medium or a process such as catalytic membrane reactors. This requires the understanding of the reaction mechanism and the knowledge of its kinetics. To date, research, mainly devoted to tin-based complexes in homogeneous catalysis and to oxides in heterogeneous catalysis, has not removed the obstacles to promote a high-performance and sustainable catalytic process. The majority of metal oxide studies deal with ceria, zirconia and cerium-zirconium mixed oxides [3-5]. A review on DMC synthesis over ceria-based catalysts is given in [6]. However, the reaction mechanism over ceria-based and related oxide catalysts is still not fully understood.

Bell et al. proposed a complete mechanism over ZrO<sub>2</sub>, based on infrared and Raman spectroscopic measurements [7,8]. The adsorption of methanol is dissociative and produces water and methoxides species [9] through the reaction with terminal- or bridged hydroxyl groups. According to [8], only the terminal methoxy species are reactive. Next, direct insertion of carbon dioxide into the terminal methoxy species takes place, yielding monomethyl carbonate (MMC). This step does not involve

bicarbonate species, which are too stable [8,9]. Less consensus is found for the last step the formation of DMC by the reaction of methanol with MMC.

This step is reported to be the rate-limiting step [10,11]. It is commonly proposed that the formation of DMC occurs by the transfer of a methyl species to a MMC species. This implies that the second methanol molecule needs a Lewis acid site to be activated. Ikeda et al. proposed the activation of methanol on a Brønsted acid site on the  $H_3PO_4/ZrO_2$  catalyst [11]. Solid NMR measurements on the catalyst, liquid NMR on the reaction products as well as DRIFT led Aresta et al. [12] to propose the intervention of methanol in the gas phase to form the DMC. DFT studies showed that the step with the lowest energy transition state is the one where two non-adsorbed methanol molecules attack the MMC via an intermolecular step. A study conducted with oxygen-18 labeled methanol (CH<sub>3</sub><sup>18</sup>OH) proposed that a methoxide species proceeds via a nucleophilic addition on MMC [13].

Recently, we have reported on zirconia doped ceria synthesized by flame-spray pyrolysis as an active and selective catalyst for the synthesis of DMC [14]. The highest activities of the  $Ce_xZr_{(1-x)}O_2$  catalysts were obtained for molar compositions x ranging between 0.4 and 0.8, but samples prepared by flame-spray pyrolysis were much more active than those prepared by co-precipitation.

The objective of this study is to trace the oxygen atoms during the synthesis reaction of DMC. Do the oxygen atoms in DMC come from the surface and the core of the catalyst (Mars - van Krevelen type mechanism), from carbon dioxide or from methanol? By identifying their origin, steps in the proposed catalytic mechanism can be eliminated or confirmed.

#### **Experimental**

Ceria–zirconia as well as pure ceria catalysts were prepared by flame spray pyrolysis as described in [14]. The flame spray pyrolysis sample, was synthesized following a protocol described in [15,16]. Aqueous metal salt solutions were prepared with desired concentration of metals. The solutions

were sprayed into a flame (up to 2200 °C) as a fine mist. High space velocities and heat radiation loss lead to extremely short residence times (milliseconds) with high temperature gradients along the flame axis up to 170 K cm<sup>-1</sup> [17]. The metal oxide atoms aggregated into nanoparticles, which were collected on a filter. For this study a sample with the composition  $Ce_{0.5}Zr_{0.5}O_2$  was used, referred to as CZ-FSP. Its BET surface area amounted to 99 m<sup>2</sup>/g. Details on its characterization and performance in DMC synthesis are reported in [14].

To check if the crystal lattice oxygen atoms of CZ-FSP participate during the reaction of DMC synthesis, the oxygen atoms of CZ-FSP where exchanged by oxygen-18 atoms. The isotopic exchange was performed in a fixed bed quartz reactor (4 mm i.d.) with 300 mg of catalyst at 750°C. The isotopic oxygen <sup>18</sup>O<sub>2</sub> (Eurisotop) has an isotopic purity of 97.5% vol. The sample was exposed to a flow of <sup>16</sup>O<sub>2</sub> and then the flow was switched to a flow of <sup>18</sup>O<sub>2</sub> by means of a 4-way valve. The atomic mass units 32, 34 and 36, representative of the oxygen isotopomers, were recorded at the reactor exit as a function of time by a mass spectrometer (Inficon). Once a stable <sup>18</sup>O<sub>2</sub> flow was observed, the reactor was cooled down and the sample was recovered. This sample is referred to as <sup>18</sup>CZ-FSP.

The evaluation of catalyst activities was carried out using a method detailed in [18]. In the case of the DMC synthesis over the <sup>18</sup>CZ-FSP sample and to minimize the use of  $CH_3^{18}OH$ , a small volume semibatch reactor (4 cm<sup>3</sup>) was used. The cell loaded with catalyst and  $CH_3OH$  was placed in an oil bath, regulated at 120°C. The carbon dioxide pressure ( $C^{16}O_2$  in all cases) was maintained during the 2-hour reaction at 50 bar by a syringe pump (Isco 250D). The measurements were performed with methanol conversions lower than 0.4%, thus far from thermodynamic equilibrium.

At the end of the reaction, the liquid phase was recovered and filtered before being analyzed by a gas chromatograph coupled to a mass spectrometer (GC-MS, Shimadzu QP 2010). Only DMC was detected as product.

The mass spectrum of the unlabeled DMC  $CH_3^{16}O(C^{16}O)^{16}OCH_3$ , with a molar mass (M.M.) of 90 g mol<sup>-1</sup> shows the highest fragment 90 amu. DMC  $CH_3^{16}O(C^{16}O)^{18}OCH_3$  has a molecular fragment at 92 amu instead of 90 amu, and DMC  $CH_3^{18}O(C^{16}O)^{18}OCH_3$  has a molecular fragment at 94 amu.

#### Results



**Figure 1.**  ${}^{16}O_2$  to  ${}^{18}O_2$  exchange experiment over CZ-FSP at 750°C.

Figure 1 shows the evolution of the oxygen isotopomers as a function of time after the switch from  ${}^{16}O_2$  to  ${}^{18}O_2$  over CZ-FSP. At first the appearance of  ${}^{16}O^{18}O$  is observed, followed a little later by  ${}^{18}O_2$ . This indicates that a hetero-exchange occurs between  ${}^{18}O_2$  gas and surface  ${}^{16}O$ , in agreement with the results in [19]. The  ${}^{16}O^{18}O$  flow goes through a maximum and then levels off to a steady-state production, which corresponds to the 2.5% of  ${}^{16}O_2$  present in  ${}^{18}O_2$ . The  ${}^{18}O_2$  flow also reaches steady-state. The exchange was then stopped. Oxygen exchange over 3 monolayers was reported in [19] for experiments over Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> at 600°C, while other authors report 5 monolayers at 750°C [20].

<sup>18</sup>CZ-FSP was then used for the synthesis of DMC with CH<sub>3</sub><sup>16</sup>OH and C<sup>16</sup>O<sub>2</sub>. During the reaction, the surface of <sup>18</sup>CZ-FSP was composed of the following: the oxygen atoms of the hydroxyl groups were

oxygen-16 atoms due to the hydroxylation of the surface after exposure to air and water contained in methanol. The crystal lattice oxygen atoms are oxygen-18 atoms exchanged over at least 3 monolayers.

The GC-MS analysis of the obtained DMC indicated that it corresponds to  $CH_3^{16}O(C^{16}O)^{16}OCH_3$ . No oxygen-18 atoms were detected in DMC nor in the water produced.

To detect whether <sup>18</sup>O of <sup>18</sup>CZ-FSP participates in the reaction and is inserted into DMC, it is necessary to ensure that the number of oxygen-18 atoms available in <sup>18</sup>CZ-FSP was in large excess with respect to the oxygen involved in the DMC synthesis. We calculated the amount of mobile <sup>18</sup>O in <sup>18</sup>CZ-FSP by assuming that the oxygen-18 atoms in <sup>18</sup>CZ-FSP were available over 3 monolayers with a density of 14 O-atoms nm<sup>-2</sup>. This average value is taken from reference [19] for a ceria-zirconia of equivalent chemical composition and specific surface area. The calculation showed that the amount of <sup>18</sup>O atoms in the <sup>18</sup>CZ-FSP sample during DMC synthesis, 2 mmol, was much larger than the 0.2 mmol of oxygen incorporated in the produced DMC. Thus, there was sufficient oxygen-18 atoms for the production of fully labeled DMC and water.

Another experiment consisted of the reaction between  $C^{16}O_2$  and  $CH_3^{18}OH$  over oxygen-16 CZ-FSP. The DMC produced was 92%  $CH_3^{18}O$  ( $C^{16}O$ ) <sup>18</sup>OCH<sub>3</sub> (M.M.=94). It was identified through the fragment of 94 amu in the GC-MS analysis and by the low intensity of the fragment in 92, representative of  $CH_3^{18}O$  ( $C^{16}O$ ) <sup>16</sup>OCH<sub>3</sub>. The other larger majority fragments were 31, 33, 47 and 61 amu, also typical of  $CH_3^{18}O$  ( $C^{16}O$ ) <sup>18</sup>OCH<sub>3</sub> with a shift of 2 amu's related to the mass of the oxygen-18 isotope.

This result is consistent with the absence of  $H_2^{18}O$  in the reaction products. Thus, the oxygen atoms of the two OCH<sub>3</sub> groups of DMC stem exclusively from CH<sub>3</sub><sup>18</sup>OH, not from the surface oxygen-16 hydroxyl groups (<sup>16</sup>OH).

#### Discussion

The absence of <sup>18</sup>O in DMC when using an oxygen-18 exchanged ceria-zirconia catalyst implies that the reaction does not proceed according to a Mars van Krevelen type redox mechanism, which consist of a two-step process where oxygen of the catalyst is reacting with one of the reactants or product intermediates, followed by a re-oxidation of the catalyst.

The use of  $CH_3^{18}OH$  over the oxygen-16 ceria-zirconia catalyst leads to almost exclusively  $CH_3^{18}O$ (C<sup>16</sup>O) <sup>18</sup>OCH<sub>3</sub> (M.M.=94). Honda et al. [13] obtained a ratio of DMC (M.M.=94) to DMC (M.M.=92) of 3.6 for DMC synthesis with  $CH_3^{18}OH$  over pure ceria.



*Scheme 1.* Sequence of reaction steps for the synthesis of DMC from carbon dioxide and methanol. Adapted from [12].

These results can be interpreted by using the reaction mechanism proposed by Aresta et al. [12], shown in Scheme 1. In Scheme 1 the  ${}^{16}$ O and  ${}^{18}$ O atoms have been labeled by a green  $\bullet$  and a red \*,

respectively. Methanol adsorbs dissociatively on a surface hydroxyl group to form a methoxy species and an unlabeled water molecule. Carbon dioxide is inserted into the methoxy species in the next step to form a monomethyl carbonate (MMC) –OCO<sup>18</sup>OCH<sub>3</sub> species. Aresta et al. [12] used crosspolarization magic-angle spinning carbon-13 nuclear magnetic resonance spectroscopy to identify the MMC – OCOOCH<sub>3</sub> species. They further showed that this species reacts with gas phase methanol, rather than methoxy species to DMC. However, they suggested the reaction path (I) to be the most likely, due to the observed reaction order in methanol that would correspond to the involvement of two methanol-derived species in the rate-controlling step. Moreover, DFT calculations of a similar system showed more favorable energetics for the tri-molecular system than the interaction with a single methanol molecule. On the other hand, Aresta et al. [12] argued that the tri-molecular mechanism may appear entropy forbidden [90]. Re-examining the different reaction routes in the light of the results of the labeled methanol experiments, excludes directly the first two routes, (I) & (II) in Scheme 1, for the conversion of the MMC,  $-OC(O)^{18}OCH_3$  species, as those routes yield H<sub>2</sub><sup>18</sup>O and only partially labeled DMC. The route (III), on the other hand, leads to the correctly labeled products DMC and water. DMC is thus formed by a nucleophilic addition of a CH<sub>3</sub><sup>18</sup>O methoxide species on MMC –OC(O)<sup>18</sup>OCH<sub>3</sub> species. Honda et al. [13] reached a similar conclusion for DMC synthesis over pure ceria.

Mixed cerium-zirconium oxides at intermediate compositions are more active than the pure oxides [80]. Zirconia doping of ceria, can promote the catalyst activity either by accelerating the ratecontrolling step or by increasing the number of active sites. Daniel measured apparent activation energies for DMC synthesis over Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> and CeO<sub>2</sub>, both synthesized by flame spray pyrolysis, of 74 and 86 kJ/mol, respectively [21], shown in Figure 2. This corresponds to approximately a 30-fold increase in activity at 140°C for the zirconia doped sample, which was observed experimentally for samples with similar surface areas [80]. The MMC species have been observed by IR spectroscopy under reaction conditions and seem to be stable intermediates. Step (III) in Scheme 1 is thus likely the rate-controlling step.



Figure 2. Arrhenius plot for the synthesis of DMC from methanol and carbon dioxide over Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> and CeO<sub>2</sub>.

Zirconia doping of ceria is known to increase the oxygen mobility [19]. It has been reported that the highest oxygen storage capacity of cerium-zirconium mixed oxides,  $Ce_xZr_{(1-x)}O_2$ , occurs for intermediate compositions 0.4 < x < 0.7 [22], just like the maximum activity for DMC synthesis [14]. However, a direct link between the oxidation state of cerium and the DMC yield has not been clearly established. According to our data, surface or lattice oxygen atoms are not participating to DMC synthesis, ruling out any causal correlation between the oxygen storage capacity and catalyst activity. A more likely explanation is that zirconia doping of ceria weakens the metal-oxygen bond thus lowering the activation energy of this step.

#### Conclusions

DMC synthesis from carbon dioxide and methanol have been studied using either an oxygen-18 labeled cerium-zirconium oxide or oxygen-18 labeled methanol. These experiments allowed to shed light on the reaction mechanism. The reaction mechanism consists of three steps: reaction between methanol and surface hydroxyl groups to form water and methoxy species. Reaction between carbon dioxide and surface methoxy species to give surface MMC species. Finally, the rate controlling step is a nucleophilic attach of methanol on the MMC species to yield DMC. The oxygen atoms in DMC stem either from methanol or carbon dioxide, but oxygen atoms from cerium-zirconium oxide do not participate in the reaction. The role of zirconia is to weaken the metal-oxygen bond of the MMC species and thus accelerate the reaction by lowering the activation energy of the last step. However, further studies are necessary to confirm this, for example through ab initio calculations.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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