Catching the surface intermediates and elucidating the redox contribution of CeO_2 during dimethyl carbonate synthesis from CO_2 and methanol

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Abstract: CeO_2 was found to be the highly efficient catalyst in direct dimethyl carbonate (DMC) synthesis from CO_2 and methanol in presence 2-cyanopyridine with excellent DMC yield (>90%) in both batch and continuous operations. By employing powerful *operando* spectroscopic approaches in conjunction with multivariate curve resolution (MCR) analysis and isotopic labeling experiments, the redox contribution of the CeO_2 catalyst material and IR fingerprints of surface intermediates were unraveled. It was observed that in gas phase DMC synthesis from methanol and CO_2, methanol acts as a reducing agent for CeO_2 whereas CO_2 behaves as an oxidizing agent thereby inducing the redox behavior in CeO_2.

Keywords: dimethyl carbonate, CeO_2, *operando* spectroscopy

1. Introduction

Owing to highly useful properties, DMC positioned to be an important molecule in several applications, such as polar solvent for paints and coatings, methylating and carbonylating agent in organic synthesis, electrolytes in Li-ion batteries, and as a fuel additive due to its high oxygen content.[1, 2] The direct methanol carboxylation reaction (**Figure 1**) represents a safer and cleaner way for DMC production, eliminating the use of toxic phosgene or CO while providing an extremely high atom efficiency based on the reaction stoichiometry.

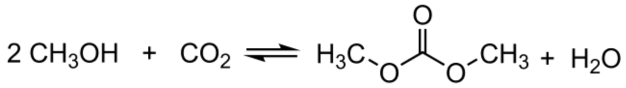

Figure 1. Direct methanol carbonylation reaction to produce DMC.

However, the reaction is severely thermodynamically-limited and efficient removal of co-product, water, is necessary to achieve high DMC yield. The most successful finding involves the use 2-cyanopyridine (2-CP) as a dehydrating agent to achieve outstanding methanol conversion and DMC selectivity over CeO_2 catalyst[3, 4]. The unique catalytic performance of CeO_2 may originate from the synergy between its acid-base properties and redox capabilities which include high lattice and surface oxygen mobility. In this work we aim at capturing the surface intermediate species leading to DMC by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and at elucidating the contribution of redox properties by XAS and Raman spectroscopy under working, *operando*, conditions. Transient techniques such as periodical concentration perturbation were utilized to highlight the reactive species signals and to observe the change in oxidation state of CeO_2. Obtained results were correlated with the product concentrations which was measured by mass spectrometry (MS).

2. Experimental

The details about chemical reagents, catalysts and experimental can be found in our earlier report [4]. A setup similar to the already presented in the literature[5] was employed for the *in situ/operando* XAS/Raman/MS measurements. The DRIFTS cell used for infrared measurements mimics the action of plug flow reactor and the design is described elsewhere[6].

3. Results and discussion

Figure 2 presents time-resolved *operando* DRIFT spectra and DMC concentration profile under a periodic concentration change of methanol (16.5 vol% in He, the first half period of 128 s) and CO_2 (the second half period of 128 s) performed at 120 °C. According to the MS signal (**Figure 1**, left), DMC was formed under the studied condition. The production level of DMC increased upon switching from CO_2 to methanol, reaching a constant level after ca. 40 s. Interestingly, the DMC production was boosted by ca. 5 times upon switching to CO_2 and gradually completely ceased with time under the flow of CO_2. The differential DRIFT spectra (**Figure 2**, right; the last spectrum of the period, i.e. at the end of the CO_2 period, was used as the background) shows the characteristic C-O stretching vibrations of bridged and terminal methoxy species appearing at ca. 1060 and 1120 cm^{-1}, respectively,[7] as positive bands (in red) when the atmosphere was switched to methanol. At the same time, several negative bands characteristic of carbonates/bicarbonates were prominently observed in the region from 1150-1800 cm^{-1} under the flow of CO_2. Careful spectral band assignment reveled that carbonates/bicarbonates formed under CO_2 atmosphere were replaced (thus the bands appear negative) by methoxy under methanol atmosphere and vice versa under CO_2 atmosphere. The nature of the intermediate species was examined by MCR analysis as well as performing the identical study using ^{13}C-labeled CO_2 and ^{13}C-labeled methanol.

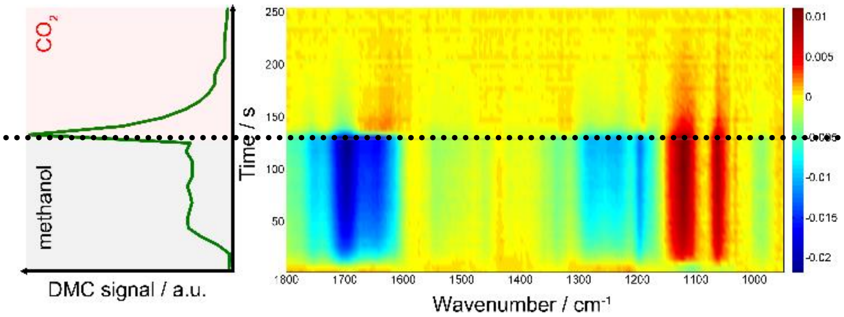

Figure 1. (left) MS signal of DMC (m/z = 59) and (right) time-resolved DRIFT spectra taken during methanol (the first half period) vs. CO_2 (the second half period) concentration perturbation experiment performed at 120 °C at 7 ml min^{-1}.

MCR analysis (data not shown) was employed to disentangle the overlapping peaks into the spectra of “kinetically pure” components (i.e. surface species). Furthermore, the oxidation state change data obtained during concentration perturbation experiments employed in *operando* Raman/XAS (data not shown) was correlated with intermediate species observed by DRIFTS to obtain meaningful mechanistic insights.

4. Conclusions

The present study shows the involvement of CeO_2 redox properties in gas phase DMC synthesis from CO_2 and methanol. While methanol acts as a reducing agent for CeO_2, CO_2 behaves as an oxidizing agent. Furthermore, a boost in DMC production is observed when CO_2 is passed over methoxy covered surface accompanying the oxidation of CeO_2. The surface intermediate species directly correlated with DMC formation was elucidated by *operando* DRIFTS with the aid of MCR analysis. It showed the feature of both methoxy and (bi)carbonates, in accordance with the reported structure of monodentate methyl carbonate (MMC). The isotopic labeling study indicated that the carbon in methyl/methoxy group of MMC strongly interacts with the CO bond of the carbonate moiety, implying that the methyl group may be delocalized around the carbonate (anion) even within the time-scale of IR spectroscopy, thus strongly coupling with the carbonate vibrations.

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