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Short communication

A thermodynamic resolution of dimethyl carbonate decarboxylation and the first example of its reversibility: Dimethyl ether carboxylation



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1. Introduction

Using a continuous bench-scale reactor loaded with zinc exchanged faujasite (Zn-FAU), we have demonstrated that dimethyl carbonate (DMC) decomposition to dimethyl ether (DME) and CO_2 is a reversible process. During the past twenty years, development of an efficient catalyst for bulk production of dimethyl carbonate (DMC) from CO₂ and methanol has been pursued given its economical interest as oxygenated fuel additive as well as for its potential as a green methylating agent and solvent [1–5]. However, catalyst development for methanol carboxylation to DMC has shown to be hindered not only by CO₂ kinetics inertia, but also by an important reaction inhibition caused by water co-production [6]. Actually, the only industrially scalable method for producing DMC from methanol and CO₂ is the water-free reaction sequence involving epoxide carboxylation to cyclic carbonate followed by transesterification with methanol producing DMC and the 1,2-diol associated to the initial oxirane [7–9]. As this DMC synthesis process also involves converting an epoxide into a 1,2-diol, the economic viability of the process is highly dependent on downstream usage of the diol, either as an addedvalue co-product from the reaction or as a feed to regenerate epoxide [10,11].

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ABSTRACT

Dimethyl carbonate (DMC) decarboxylation and dimethyl ether (DME) carboxylation was found to be a system under equilibrium in which CO_2 is the cornerstone. DMC decarboxylation to DME and CO_2 was thermodynamically and kinetically resolved, which allowed obtaining conditions in which DME carboxylation is thermodynamically favourable. Subsequent demonstration of DME carboxylation represents the first example of CO_2 insertion in an aliphatic ether function. This study was carried out using a continuous fixed bed reactor loaded with zinc-exchanged faujasite catalyst, design to mimic the equilibrium mechanism of CO_2 hydration by the enzyme carbonic anhydrase.

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Herein, we present the thermodynamic resolution of DMC decarboxylation to DME and the first example of DME carboxylation to DMC (Eq. (1)). DME carboxylation is a novel water free and direct synthetic path to DMC from CO₂ with 100% atoms efficiency.

$$\sim_{0}$$
 + co_{2} cat, Δ 0 (1)

DMC decarboxylation to DME and CO₂ is a known process and its reversibility is found to be the results of a temperature dependant chemical equilibrium, as previously demonstrated in cvclic carbonates synthesis [12–15]. The catalyst used in this work is a zinc-loaded faujasite at its near full exchange capacity. It has been designed in order to mimic the zinc prosthetic group and reactivity of the active site of the enzyme carbonic anhydrase (CA). The metalloenzyme induces CO₂ hydration through equilibrium displacement promoted by a tri-coordinated Zn^{II} porphyrin, aided by a histidine residue that acts as proton shuttle between the reaction site and the bulk solution [16]. The faujasite framework consists of sodalite cages connected through hexagonal prisms, which result in a structure made of 4T and 6T rings (T for tetrahedral atoms) with diffusion channels of 7.4 Å aperture [17– 19]. Previous work on single crystals XRD characterization of the zinc-exchanged faujasite has demonstrated that preferential location of metals is at a first instance in the sodalite cages, then at the surface of supercages 6T rings. Characterization of Zn-FAU synthesized through wet impregnation as in this work was also found to have abundance of zinc located 6T ring sites [20]. These









Fig. 1. Zinc environment in (a) carbonic anhydrase metalloporphyrin and (b) zinc exchanged faujasite 6T ring.

zinc located 6T ring sites are accessible to substrates for reaction and as in the *CA* active site; the acidic zinc centre is in a three coordination state [20,21]. The electron density and geometrical analyses of the *CA* active zinc centre and substrate accessible zinc exchanged faujasite 6T rings site are given in Fig. 1 and Table 1. The analysis of the *CA* active site was carried out directly on the crystal structure of the enzyme while the zinc-loaded faujasite 6T ring site has been artificially reconstituted through DFT structure optimization at the ONIOM(M06/6-31g(d),SBKJC VDZ:PM6) theory level. Charges of both sites were then obtained by full DFT single point calculation. Larger cluster and description of the method used for obtaining these structures is provided in the supporting information.

The acid strength of the faujasite material is known to activate DME in a similar fashion as H₂O activation by the metallo-enzyme. The induction of CO₂ hydration by the metalloenzyme is initiated by the activation of a water molecule to reversibly produce a zinc hydroxide centre in which CO₂ insertion occurs, while a proton is taken away by a proximal basic function [22–24]. Comparatively, the first steps of numerous heterogeneous reactions such as hydrolysis, carbonylation, and DTO involving a gas flow of DME at the surface of zeolites, is the DME acid-promoted C–O bond cleavage resulting in the formation of a surface methoxonium and adsorbed methanol intermediate [25–27]. Consequently, promoting the same reaction pattern at the surface of zinc-exchanged faujasite potentially results in the reversible formation of adjacent zinc-methoxide and surface methoxonium active complex, analogue to the *CA* key intermediates in which CO₂ insertion occur.

2. Experimental

2.1. Catalyst synthesis

The catalyst was prepared from zeolite Y CBV 600 (faujasite) in his hydrogen cation nominal form with SiO₂/Al₂O₃ ratio of 5.2, purchased from Zeolyst International. Zinc(II) was loaded in CBV 600 using $Zn(NO_3)_2$ ·6H₂O salt with purity higher than 98%, purchased from Sigma Aldrich. Zn-FAU was prepared by Brønsted acid sites neutralization using the incipient wetness method, a fully scalable synthesis procedure which does not require solvents other than water. Specifically, to a 1 L round bottom flask containing 400 mL of deionised water at 333 K, were gradually added CBV 600 (75 g, 0.322 mol of Al, 1 equiv.) while stirring under air. The resulting solution were vigorously stirred at 333 K during 2 h, then Zn(NO₃)₂·6H₂O (38.32 g, 0.129 mol Zn, 0.45 equiv.) was added slowly. The resulting mixture was stirred overnight at 333 K under air. Without any filtration, water was removed under vacuum (-32 PSIG) at 363 K, resulting in a white thick and solid crust. The solid has been kept in the 1 L round bottom flask and place in an air stationary oven at 105 °C for 24 h. The solid has then

Table 1

Bond length and charge density of (a) carbonic anhydrase Zn porphyrin and (b) zinc exchanged faujasite 6T ring.

(a)	Zn	N(1)	N(2)	N(3)
Charge ^a	0.577	-0.491	-0.481	-0.534
Zn ^b	2.06 ^c	2.06	2.03	2.08
(b)	Zn	O(1)	O(2)	O(3)
Charge ^a	0.950	-0.884	-0.901	-0.887
Zn ^b	1.92°	1.90	1.93	1.93

^a Mulliken charges.

^b Distance (Å).

^c Average distance (Å) to ligand.

been transfer in a 5 in. diameter quartz tube and place in a high temperature tube furnace and calcinated at 723 K under a 1 L min⁻¹ air flow. The calcinations procedure which involves slow temperature increase ramp was completed with a final heating stage of 4 h at 723 K, which is slightly above the zinc oxide Hüttig temperature, temperature at which ZnO mobility is occurring on a catalytic surface [28]. The post calcinations material (Zn-FAU) was still a white thick and solid crust which was then crushed and sifts. The particles with size fractions ranging from 1.4 to 2.5 mm were collected (85.2 g) and stored under dry atmosphere for characterization and catalyst activity measurement. The materials were characterized all along the synthesis procedure using XRD, XRF, SEM and SAXS analysis. The different characterization procedures are provided in supporting information.

2.2. Reactor

Catalyst testing was carried out using a bench-scale reactor. The setup consisted of a tubular fixed bed reactor with internal diameter of 1905 mm, where the catalyst was immobilized between two layers of inert material, silicon carbide. The catalyst bed temperature was controlled using a tube furnace with homogeneous temperature gradient, and internal temperatures were monitored by a thermocouple with the head carefully placed in the middle of the reactive zone. Temperature and pressure were graphically monitored at several points of the reactor, to guarantee that reagents were reaching the catalyst as gaseous species and that no pressures build up was occurring. The CO₂ flow was controlled using a high precision mass flow controller, while liquefied DME or DMC was pumped continuously and subsequently vaporized in the heated inlet stream. The reactor outlet composition was quantified using gas chromatography system, the AGILENT 7820A, equipped with a FID detector and a DB624 column. GCMS, AGILENT 7890A equipped with VL MSD triple axis detector 5975C and DB624 column, was used for outlet stream composition analysis.

2.3. Catalyst activity measurements

Typical procedure for DMC decarboxylation experiments consisted to pre-heat the reactor inlet, outlet and catalyst containing area under a $1 \text{ L} \text{min}^{-1} \text{ N}_2$ flow. The inlet and outlet stream were heated to 398 K and the catalyst internal temperature was set to a desired temperature. Once the reactor temperature, pressure and flow were stabilized at the desired reaction conditions, liquid DMC was added continuously in the inlet stream at a rate of 0.02 mL_(liq) min⁻¹ using a diaphragm pump.

Dimethyl Ether carboxylation experiments was carried out following a similar procedure as describe for DMC decarboxylation. 1.5 $L_{(gas)} min^{-1}$ of CO₂ was used as vector gas during pre-reaction setup conditioning and liquefied DME was added using a high pressure syringe pump. Typically, the reactor inlet and outlet

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