

# Direct CO<sub>2</sub>-to-DME hydrogenation reaction: New evidences of a superior behaviour of FER-based hybrid systems to obtain high DME yield



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## ABSTRACT

The catalytic behaviour of Cu-Zn-Zr/zeolite hybrid systems, in which metallic and acidic functionalities were combined at level of single grain, was evaluated in the direct DME production by CO<sub>2</sub> hydrogenation. Catalysts were prepared by co-precipitation of the metals precursors in a slurry of three home-made powdered zeolites, characterized by different dimensional frameworks (*i.e.*, MOR, FER, MFI). The experiments were carried out in a fixed bed reactor operating at 5.0 MPa and temperature ranging from 200 to 260 °C. By appropriate physico-chemical characterization of systems it was revealed that morphology of zeolite crystallites significantly affects the surface distribution of metal-oxides and the nature of active sites created during the co-precipitation step. The FER zeolite was seen to ensure a better dispersion of cluster oxides, favouring the generation of Lewis basic sites for CO<sub>2</sub> activation along with a higher availability of Brønsted acid sites for the MeOH-to-DME dehydration step. The catalytic results clearly evidenced a net difference in behaviour among the investigated hybrid systems, both in terms of CO<sub>2</sub> conversion and product distribution. Peculiar structure-activity relationships highlighted the superior performance of CuZnZr-FER catalyst, allowing to reach the highest DME productivity value ( $\approx 600 \text{ g}_{\text{DME}}/\text{kg}_{\text{cat}}/\text{h}$ ), as the consequence of better efficiency in mass transferring ensured by neighbouring active sites involved in the reaction mechanism. The stability test evidenced a progressive deactivation not associated to coke deposition or metal sintering, but mainly to water formation which negatively affects the behaviour both of metal-oxide and acid sites controlling the DME synthesis rate.

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## 1. Introduction

The production of dimethyl ether (DME) by hydrogenation of CO<sub>2</sub> is an issue that recently is receiving particular attention [1–3]. Direct synthesis of DME from CO<sub>2</sub> was reported to have major thermodynamic advantages over the two step process, involving consecutive methanol synthesis and dehydration reactions. Indeed, the catalytic hydrogenation of CO<sub>2</sub> for direct synthesis of dimethyl ether can markedly improve the conversing of CO<sub>2</sub> because the dehydration of methanol into DME can break the thermodynamic balance of methanol synthesis [3]. As well known, in order to obtain DME *via* this direct reaction it is necessary that

the catalyst employed possesses a multi-functionality, as the reaction proceeds through the formation of methanol and subsequent dehydration to DME [3–12]. In general, first methanol is generated by interaction of activated hydrogen and CO<sub>2</sub> on metal-oxide sites, while DME is then formed by dehydration of methanol (MeOH) on acid sites [7,13–16]. Generally, a mechanical mixture of mixed oxides (containing Cu as active species for the synthesis of methanol) and a zeolite, typically ZSM-5 [17–30], have been mainly proposed as an effective catalytic system. In particular, some fundamental aspects have been indicated as crucial for high process productivity: i) the zeolite must be stable in presence of water; ii) the formation of olefins should be inhibited; iii) the acid sites must be well distributed and of suitable strength [1,25,31–38]. Montesano et al. [39] have recently published some results using different zeolites (*i.e.*, Theta-1, ZSM-23, ferrierite,

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mordenite, ZMS-5) in mixture with a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol catalyst for the conversion of syngas into DME. The authors report a superior catalytic performance in presence of ferrierite and unidirectional zeolites at 250–270 °C and 3.0 MPa, thanks to the topology of ferrierite that limits the formation of hydrocarbons, possibly by providing a preferential path for the diffusion of small reactants and products (i.e., methanol and dimethyl ether).

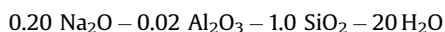
However, considering the limitations encountered using a mechanical mixture [40], recently attention has been paid on the possibility of preparing multimetallic-acidic single grain hybrids to enhance the mass transfer phenomena, so that the multifunctionality necessary for the reaction is grain-to-grain ensured [31]. Bonura et al. have recently published some interesting results demonstrating that a “homogeneous” multi-site system is more efficient in terms of CO<sub>2</sub> conversion and DME/MeOH yield with respect to a mechanical mixture [40]. The authors have motivated this finding by assuming that the system promotes both the formation of methanol, due to a suitable extent of metal-oxide interfacial area, and the fast transport of methanol on acid sites (easier accessibility of the acid sites of the zeolite), where the dehydration to DME occurs [31,40]. It was also shown that the acidity of the systems, naturally, plays a determining role in the production of DME; however it is preferable to have a system characterized by acid sites homogeneously distributed on surface; normally, too strong acid sites do not lead to the formation of DME [14,25,31,41–44]. Here, comparative results obtained on Cu-Zn-Zr/zeolites hybrid systems are discussed, with the aim to better clarify the role of zeolites characterized by different structure and acidity. Indeed, recently we have already reported some results obtained in the presence of hybrid systems [45], but considering the difficulty to obtain quantitative information about the metal-oxide interface (the surface region already proposed as key center where CO<sub>2</sub> activates [28,30,31]), along with the need to give more consistency to the observed “homogeneous distribution of metal-oxide sites on FER”, now the MS prompts to individuate other “more tangible” indicators controlling the catalytic performance, aiming at giving more strength to conclusions previously emerged too provisional and speculative and providing direct relationships related to the main features and nature of active sites involved the CO<sub>2</sub>-to-DME hydrogenation reaction.

## 2. Experimental

### 2.1. Preparation of MOR, FER and MFI zeolites

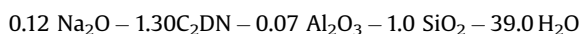
Three zeolite structures with different dimensional framework characteristics (MOR, FER, MFI) were synthesized, according the following procedures.

The mono-dimensional MOR structure was synthesized without structure-directing agents (SDA) starting from the following molar composition:



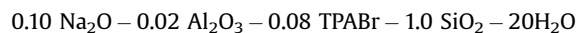
Sodium aluminate and precipitated silica were used as aluminium and silica sources, respectively. The synthesis gel was left in a PTFE-lined stainless steel autoclave at 175 °C for 120 h in static conditions, while the acidic form was obtained after two cycles of ionic exchange with NH<sub>4</sub>Cl 1 M (1 h each) and calcination at 550 °C.

The bi-dimensional FER structure was prepared from the following gel (molar composition), using ethylenediammine (C<sub>2</sub>DN) as template [46]:



while sodium aluminate and LUDOX<sup>®</sup> AS-40 were used as aluminium and silica sources, respectively. After 2 h stirring at room temperature, the synthesis gel was transferred in a PTFE-lined stainless steel autoclaves at 175 °C for 10 days in tumbling conditions. After the synthesis completion, the sample was filtered with distilled water and calcined in air at 550 °C for 8 h. The acidic form was obtained after two cycles of ionic exchange with a solution 1 M of NH<sub>4</sub>Cl (1 h each), followed by calcination at 550 °C.

The three-dimensional MFI structure was prepared following the synthesis procedure published elsewhere [47], starting from the following synthesis gel (molar composition):



The crystallization was carried out in 150 mL PTFE-lined stainless steel autoclave in static conditions at 175 °C. After 96 h of crystallization, the solid phase was separated from the liquid by filtration, washed several times with distilled water and dried at 100 °C overnight. In order to give the acidic properties to the catalyst, the samples was calcined at 550 °C for 8 h and a double proton exchange procedure was performed by using 100 mL per catalyst gram of aqueous solution 1 M of NH<sub>4</sub>Cl refluxed at 80 °C. The ammonia was then eliminated by calcination, obtaining the final H-MFI form.

### 2.2. Synthesis of single grain hybrid catalysts

The procedure adopted for the preparation of the single grain hybrid catalysts consists in the *in situ* combination of CuZnZr methanol synthesis precursors with the preformed powdered zeolites. Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O (in a Cu/Zn/Zr atomic ratio of 60/30/10) were solubilized in ethanol and coprecipitated by oxalic acid (gel-oxalate coprecipitation) at room temperature under vigorous stirring [31] in a solution containing the zeolite finely dispersed (particle size <100 nm), with a final CuZnZr:zeolite weight ratio of 2:1. The solids were stirred for 3 h, aged overnight, then filtered and dried at 95 °C for 16 h. The calcination in muffle of the dried powders was performed according the following stepwise procedure: 1) 150 °C for 1 h; 2) 200 °C for 1 h; 3) 250 °C for 1 h; 4) 300 °C for 1 h; 5) 350 °C for 4 h.

### 2.3. Catalysts characterization

#### 2.3.1. Total surface area measurements

The textural properties of catalysts were determined by physical adsorption measurements of nitrogen to its boiling point (–196 °C), using a Micromeritics ASAP 2020 gas adsorption device. The isotherms were elaborated for assessment of surface area (SA) and porosity (PV), with the micropore volume (MV) determined by the *t*-plot approach.

#### 2.3.2. X-rays diffraction (XRD) measurements

XRD patterns of catalysts were obtained by a Philips X-Pert diffractometer operating at 40 kV and 30 mA, employing the Ni β-filtered Cu K<sub>α</sub> radiation (λ = 1.5406 Å) in the 2θ range 5–80°. Identification of XRD patterns was made on the basis of the JCPDS database, while the metal particle size was determined by Scherrer equation assuming a Gaussian shape of the peaks.

#### 2.3.3. Chemical composition and scanning electron microscopy (SEM) analysis

The chemical composition of the samples was determined by ICP-MS (Perkin-Elmer DRC-e), while their morphology along with element distribution was studied by SEM-EDAX analysis (Philips XL-30-FEG).

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