



Acidity control of zeolite functionality on activity and stability of hybrid catalysts during DME production via CO₂ hydrogenation

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ABSTRACT

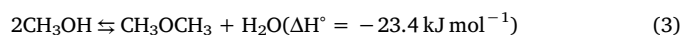
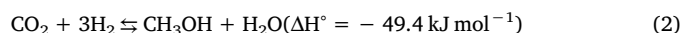
The catalytic behaviour of a CuZnZr-FER hybrid catalyst was assessed in the direct CO₂-to-DME hydrogenation reaction, considering the effects of structural and surface properties induced on the system by homemade ferrierite samples at different acidity and grain size. Notwithstanding a comparable initial activity under the adopted experimental conditions ($T_R = 220\text{--}260\text{ }^\circ\text{C}$; $P_R = 3.0\text{ MPa}$; GHSV = 8800 NL/kg_{cat}/h), the investigated catalyst samples exhibited a different behaviour in terms of stability, with a progressive decay with time mostly marked on the hybrid containing ferrierite at larger acidity. Irrespective of the zeolite grain size, TEM analysis showed a low tendency of catalysts to form carbon deposits, while the comparison of surface properties of “fresh” and “used” samples evidenced a significant metal sintering occurring during reaction, proportional to the Si/Al ratio. The loss of metallic surface area was mainly connected to water formation, as proved in the measurements at high contact time in which a larger net drop between initial and final DME yield, resulting from a higher partial pressure of water, was recorded.

1. Introduction

Dimethyl ether (DME) is a biodegradable and environmentally friendly compound, usable as an alternative to conventional fossil fuels due to its positive profile of combustion, high cetane number as well as reduced combustion noise during engine warm-up [1–10]. The conventional synthesis of DME via methanol (MeOH) dehydration has the drawback of being highly dependent on the price of methanol [4,11–15]. In addition, methanol production from synthesis gas is limited by thermodynamic constraints and, to ensure an acceptable overall conversion, a high pressure and a large recycle stream to the reactor is required. The direct DME synthesis overcomes these restraints, leading to higher per-pass CO conversions and higher DME productivity. However, starting from syngas, a lower carbon efficiency is accomplished, being produced significant amounts of CO₂ through the fast water gas shift reaction (WGS) between carbon monoxide with released water [16–27].

For all these reasons, the direct DME synthesis from CO₂ hydrogenation (Eq. (1)), integrating the methanol synthesis (Eq. (2)) and its dehydration to DME (Eq. (3)), appears to be a much more attractive approach [11,28–35], because recycling of ‘waste’ CO₂ through

hydrogenation can effectively close the carbon loop [6,36,37].



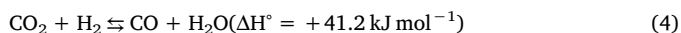
Moreover, if the need for one single reactor can reduce the investment and operational costs, the possibility to exploit emerging technologies utilizing solar energy, wind power, hydropower or biomass, can provide renewable hydrogen at large scale yielding a sustainable process from an environmental and energy point of view [7,38–40].

The main problem limiting the industrial application of the direct synthesis is represented by CO₂ stability, so that, to overcome the activation energy barrier, operation under high pressure ($\geq 3\text{ MPa}$) and temperature (220–260 °C) and in presence of appropriate multi-functional hybrid catalysts is required, leading to conversion values below 30% and maximum DME selectivity of 50% [7,29,41–64]. Apart from the need of optimal experimental parameters, the crucial issue for preparing a high-active hybrid catalyst is optimizing the formulation and interaction of the two functional metal-oxide(s) and acidic components, respectively capable to form and dehydrate methanol. On this

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account, although Cu can work alone as a methanol synthesis catalyst, its activity is typically boosted by the interaction with ZnO, which on its own has only negligible catalytic activity. In fact, ZnO exerts various peculiar functions, mainly devoted to enhance metal dispersion or Cu-ZnO interfacial area [7,8]. So, the Cu-ZnO system has emerged as a reference system in the catalytic hydrogenation of CO₂, but the need for an improved activity-selectivity pattern has prompted several studies towards a much more complex catalyst design, so to realize multi-metallic systems more active than bimetallic catalysts in the formation of MeOH, to be then dehydrated into DME. Specifically, the addition of ZrO₂, instead of classical Al₂O₃, was found to improve catalyst stability under various reaction conditions, due to a better water tolerance of zirconia in respect of alumina [30,50,55,61]. In our previous investigations [65–67], a superior catalytic performance was demonstrated on hybrid catalysts based on oxides of copper, zinc and zirconium embedding ferrierite (FER) as the dehydration component, considering that the generation both of metal-oxides and acid sites in a single catalyst grain leads to an increased once-through conversion of CO₂ compared to conventional mechanical mixing of a methanol synthesis catalyst and a zeolite, enhancing the forward reaction and limiting the CO₂ consumption via the reverse-WGS reaction (Eq. (4)), owing to a favorable topology facilitating easy diffusion of reactants and products among neighboring metal-oxide-acid sites [66,67]:



Considering that the current approach to DME synthesis from CO₂ hydrogenation is mainly focused on the development of increasingly innovative catalytic materials, however new studies are still necessary about catalyst lifetime, in the perspective of scale-up from lab to pilot plant operation. Therefore, although we already deemed a balanced density of surface sites to be crucial for high DME productivity [59,67,68], in this paper the effects of a variable acid capacity of ferrierite-type zeolites on the activity and long term stability of hybrid CuZnZr-FER systems are elucidated, with the aim of establishing the strategies for improving the catalyst performance in the synthesis of DME in a single step via CO₂ hydrogenation.

2. Experimental section

2.1. Preparation of the hybrid systems for the CO₂-to-DME hydrogenation reaction

Preliminarily, three FER-type zeolites were prepared by tuning the alumina amount so to obtain samples characterized by the following Si/Al molar ratio: 8, 30 and 60. Concerning the FER8 sample, the synthesis gel was prepared by mixing 0.15 g of sodium hydroxide (ACS reagent, ≥99% pellets, Aldrich) with 1.20 g of NaAlO₂ (43 wt% Na₂O, 54 wt% Al₂O₃, 3 wt% H₂O) and 34.22 g of distilled water. The solution was stirred for 1 h and then 5.41 g of pyrrolidine (99%, Sigma Aldrich) were dropwise added in 30 min. At last, 19.04 g of Ludox AS-40 (40 wt% SiO₂, Aldrich) were solubilized in the gel, followed by stirring (2 h) at room temperature. The crystallization of the sample was completed in 60 mL PTFE-lined stainless steel autoclave in static conditions at 165 °C. After 72 h under tumbling conditions, the solid phase was separated from the liquid by filtration, washed several times with distilled water and dried at 100 °C overnight. As for the FER30 sample, 127.12 g of H₂O were mixed with 1.48 g of NaOH and 0.89 g of NaAlO₂; the obtained solution was stirred for 1 h to completely dissolve reagents and then 5.41 g of pyridine (VWR, AnalaR NORMAPUR) were dropwise added in 30 min. Then, 19.65 g of silica fumed (SA = 200 ± 25 m²/g, Aldrich) were added in the gel upon a patient spatulation for 1 h. The crystallization was carried out in 150 mL PTFE-lined stainless steel autoclave in static conditions at 165 °C for 170 h. Afterwards, the solid phase was recovered by filtration, washed several times with distilled water and dried at 100 °C overnight. FER60 was prepared similarly to

FER30, by using only 0.45 g of NaAlO₂ and a crystallization time as long as 120 h. Nano-FER was prepared by adding sodium lauryl sulphate (SLS) to a synthesis gel prepared according to the method adopted for the synthesis of FER8 sample, using a SLS/Al₂O₃ molar ratio of 0.3. In a typical synthesis, sodium aluminate, NaOH, pyrrolidine and sodium lauryl sulphate were dissolved in distilled water and the mixture was stirred until complete dissolution of components. Afterwards, colloidal silica was dropwise added to the solution and the gel was stirred for 1 h. The obtained gel transferred in a 80 mL autoclave and left for 72 h at 180 °C in a tumbling oven (rotation speed: 15 rpm). In order to obtain the acid form, the samples were calcined at 550 °C for 8 h and a double proton exchange procedure was performed by using an aqueous solution 1 M of NH₄Cl (100 mL/g) refluxed at 80 °C. The ammonia was then eliminated by calcination, obtaining the final H-FER form at different Si/Al ratios.

Cu(NO₃)₂·2.5H₂O, Zn(NO₃)₂·6H₂O and ZrO(NO₃)₂·nH₂O (in a Cu/Zn/Zr atomic ratio of 60/30/10) were solubilized in ethanol and co-precipitated by oxalic acid at room temperature under vigorous stirring [55] in a solution containing the zeolite finely dispersed (particle size < 100 μm), with a final CuZnZr/ferrierite weight ratio of 1:1. The precipitate was stirred for 3 h, aged overnight, then filtered, dried at 95 °C for 16 h and calcined at 350 °C for 4 h, according to the stepwise procedure elsewhere reported [69].

2.2. Catalysts characterization

The textural properties of the “fresh” catalysts (reduced for 1 h under pure H₂ at 300 °C and then passivated at room temperature for 2 h under a 2% O₂/N₂ mixture) 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 the assessment of surface area (SA), with the micropore volume (MV) determined by the *t*-plot approach.

XRD patterns of the investigated catalysts (the “used” samples were cooled at room temperature under the prevailing reducing atmosphere of the reaction mixture and then passivated as above to minimize the change of phases in *ex-situ* analysis) were obtained by a Philips X-Pert diffractometer operating at 40 kV and 30 mA, employing the Ni β-filtered Cu K_α radiation (λ = 1.5406 Å) in the 2θ range 5–80°. Identification of XRD patterns was made on the basis of the JCPDS database.

The chemical composition of the samples was determined by ICP-MS (Perkin-Elmer DRC-e), while SEM analysis (FEI model Inspect) was carried out to study the morphology of the investigated catalyst samples.

Copper surface area (MSA) and dispersion (*D*_{Cu}) values were obtained by “single-pulse” N₂O-titration measurements at 90 °C. Before measurements the samples were reduced in situ at 300 °C in flowing H₂ (100 stp mL/min) for 1 h, then “flushed” at 310 °C in nitrogen carrier flow (15 min) and further cooled down at 90 °C. MSA and *D*_{Cu} values were calculated assuming a Cu:N₂O = 2:1 titration stoichiometry and a surface atomic density of 1.46 × 10¹⁹ Cu_{at}/m², while, assuming a spherical shape of Cu particles, the average particle size (*d*_{Cu}) was obtained from the conventional formula: *d*_{Cu} (nm) = 104/*D*(%) [59].

The acid capacity both of bare zeolites and hybrid catalysts was determined by temperature programmed desorption of ammonia (NH₃-TPD). Before TPD experiments, the zeolite samples (~50 mg) were placed in a linear quartz micro-reactor (*l*, 200 mm; *i.d.*, 4 mm) and flushed at 500 °C under He atmosphere (100 STP mL/min) for 30 min. The hybrid catalysts, instead, were preliminarily reduced by flowing hydrogen (100 STP mL/min) at 300 °C for 1 h. Afterwards, both zeolites and hybrid catalysts were saturated at 150 °C for 60 min in flow of a gas mixture containing 5 vol.% of NH₃/He, at a total flow rate of 25 mL/min. Then, the samples were purged in helium flow until a constant baseline level was attained. TPD measurements were performed in the temperature range 100–700 °C at a rate of 10 °C/min using helium (25

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