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Catalytic features of CuZnZr–zeolite hybrid systems for the direct CO₂-to-DME hydrogenation reaction

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ABSTRACT

The direct hydrogenation of CO₂ to dimethyl ether (DME) has been studied in a fixed bed reactor, in presence of supported CuZnZr/zeolite hybrid catalysts. To study the effects of zeolite topology on catalyst performance, two different home-made zeolite structures (i.e., FER and MOR) were used as carriers during gel-oxalate coprecipitation of CuZnZr precursors. The hybrid FER-based catalyst showed a very good activity-selectivity pattern at 5.0 MPa, also exhibiting an interesting DME productivity (STY, 752 g_{DME}/Kg_{cat}/h), with no coke formation under the adopted experimental conditions (*T_R*, 280 °C; GHSV, 8800 NL/Kg_{cat}/h). The presence of well dispersed metal-oxide clusters of the precursors on the 2-D zeolite framework of FER was indicated as a key factor to realize a more efficient mass-transferring of MeOH from CuZnZr sites to zeolite surface, favoring so the formation of DME with higher yields than obtained using MOR as support.

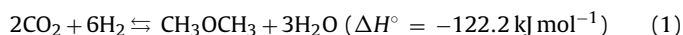
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1. Introduction

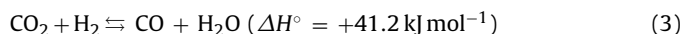
The hydrogenation reaction represents one of the most attractive options for chemical activation of carbon dioxide, offering a good opportunity for a sustainable development in energy and environmental sectors. In fact, this reaction not only contributes to reduce the increasing amount of CO₂ in the atmosphere, but it also allows to produce fuels and valuable chemicals [1]. Hydrogen supply for the chemical recycling of CO₂ could be ensured either by continuing to exploit the current fossil sources (mainly natural gas) or from renewable sources (sun, wind, etc. . .) providing, for example, energy for water electrolysis [2,3].

In this perspective, the synthesis of dimethyl ether (DME) from CO₂ hydrogenation is receiving growing attention for its potential as an alternative fuel in the automotive field [4]. In particular, the feasibility of a direct process for the production of DME from CO₂-H₂ mixtures can ensure a lower thermodynamic limitation in respect of the conventional two-step process, so reducing invest-

ments and operational costs [5–9]. In the direct CO₂ hydrogenation process, the net reaction is given by Eq. (1):



From a thermodynamic point of view, a decrease in reaction temperature or an increase in reaction pressure should favor the synthesis of DME. However, from a kinetic point of view only an increase of reaction temperature above 240 °C facilitates the CO₂ activation rate, the formation of DME being paralleled by the competitive formation of methanol (Eq. (2)) or carbon monoxide (Eq. (3)) [10,11]:



Therefore, a highly selective catalyst, characterized by specific active sites, is required to avoid the formation of undesired by-products [11,12]. Generally, after methanol is generated over a metal-oxide catalyst functionality, it is immediately dehydrated over a neighbouring acidic site, thereby enhancing the forward reaction and limiting the CO₂ consumption via-RWGS reaction [11,13–17]. The direct catalytic hydrogenation of CO₂ into DME is typically performed in presence of physical/mechanical mixtures between a Cu-based methanol synthesis catalyst (usually, CuO–ZnO–Al₂O₃ or CuO–ZnO–ZrO₂) [5,6,9,11,13,14,16,18–25] and a solid acid catalyst, such as γ -Al₂O₃, silica–alumina (less or more

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modified) or different types of zeolites [11,16,26–29], responsible for methanol dehydration.

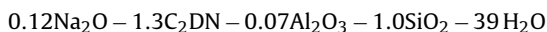
In this paper, the performance of hybrid CuZnZr–zeolite systems for the one step synthesis of DME from CO₂–H₂ mixtures is described, considering the opportunity to integrate at nanoscale level the methanol-synthesis and methanol-dehydration functionalities during the catalyst preparation, so to fulfill a more uniform distribution of the active sites. Two home-made zeolites, ferrierite (FER) and mordenite (MOR), have been synthesized as metal-oxide carriers, in order to determine how acidity, surface area, microporosity or metal-oxide loading can affect the catalyst productivity to DME.

2. Experimental

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

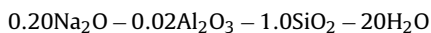
The procedure adopted for the preparation of the hybrid systems consists in the combination of a CuZnZr methanol catalyst with two different home-made zeolite structures: ferrierite (FER) and mordenite (MOR). In particular, in the attempt to merge the catalytic functionalities necessary for the direct CO₂-to-DME hydrogenation reaction, so that the two parent catalysts were not distinguishable anymore, 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 coprecipitated by oxalic acid at room temperature under vigorous stirring [30] in a solution containing the zeolite finely dispersed (particle size <100 μm), with a final CuZnZr:zeolite weight ratio of 2:1. The solid was stirred for 3 h, aged overnight, then filtered, dried at 110 °C for 16 h and calcined at 350 °C for 4 h, according to the stepwise procedure elsewhere reported [31].

The FER structure was prepared from the following gel (molar composition) using ethylenediamine (C₂DN) as template [32]:



while sodium aluminate and LUDOX® 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 NH₄Cl (1 h each), followed by calcination at 550 °C.

The MOR structure was synthesized without structure-directing agents (SDA) according to the following molar composition:



using sodium aluminate and silica precipitated 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, followed by acidification of the solid in the same way of FER.

2.2. Catalysts characterization

2.2.1. Total surface area (S_{BET}) 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 (V_{micro}) determined by the *t*-plot approach.

2.2.2. X-ray fluorescence (XRF)

The analytical composition of catalysts was determined by X-ray fluorescence analysis, using a Bruker AXS-S4 Explorer spectrometer, equipped with a Rhodium X-ray source (Rh anode and 75 μm Be-window), a LiF 220 crystal analyzer and a 0.12° divergence collimator.

2.2.3. 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 Kα radiation ($\lambda = 1.5406 \text{ \AA}$) 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.

2.2.4. Chemical composition and SEM analysis

SEM-EDAX analysis was carried out to study the morphology both of the crystalline phase of the zeolites (FEI model Inspec) and of the hybrid catalysts (Philips XL-30-FEG) as well as to analyze the atomic composition on the examined surface (EDAX, Oxford 6587). The aluminum content of the zeolite structures was also verified by ICP-MS (Perkin–Elmer DRC–e).

2.2.5. N₂O titration measurements

Copper surface area (S_{Cu}) 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. S_{Cu} and D_{Cu} values were calculated assuming a Cu:N₂O = 2:1 titration stoichiometry and a surface atomic density of $1.46 \times 10^{19} \text{ Cu}_{\text{at}}/\text{m}^2$.

2.2.6. Temperature programmed desorption measurements

Surface concentrations of acidic sites were determined by temperature programmed desorption of ammonia (NH₃-TPD). Before TPD experiments, the catalysts (~50 mg) were reduced, at atmospheric pressure, by flowing hydrogen (60 STP ml/min) in a linear quartz micro-reactor (*l*, 200 mm; i.d., 4 mm) from room temperature to 300 °C at a heating rate of 10 °C/min. Then, the samples were maintained under hydrogen flow at 300 °C for 30 min. After cleaning with helium, the samples were saturated for 60 min in flow of a gas mixture containing 5 vol.% of NH₃/He at 150 °C, 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 100–600 °C at a rate of 10 °C/min using helium (25 STP ml/min) as carrier flow. The evolved ammonia was detected by an on-line thermal-conductivity detector, calibrated by the peak area of known pulses of NH₃.

2.2.7. Transmission electron microscopy (TEM) analysis

A Philips CM12 instrument equipped with a high-resolution camera was used to acquire and elaborate TEM images. Powdered samples were dispersed in 2-propanol under ultrasound irradiation and the resulting suspension put drop-wise on a holey carbon-coated support grid.

2.3. Catalytic tests

The catalytic activity in CO₂-to-DME hydrogenation reaction was investigated in a fixed-bed stainless steel reactor (i.d., 4 mm; *l*, 200 mm) at temperature ranging from 200 to 280 °C and a total pressure of 5.0 MPa (GHSV = 10,000 NL_{g,cat}^{−1} h^{−1}; CO₂/H₂/N₂ = 3/9/1). Prior to each test, the catalyst was reduced in situ at 300 °C for 1 h in pure hydrogen flow at atmospheric pressure. The reaction stream was analyzed by a GC equipped with a two-column separation system connected to a flame ionized

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