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Hybrid $Cu–ZnO–ZrO_2$/H-ZSM5 system for the direct synthesis of DME by CO_2 hydrogenation

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ABSTRACT

One-step CO_2 hydrogenation reaction to dimethyl ether (DME) was studied on a hybrid system characterized by different reactor bed configurations (physical mixing, dual-bed and mono-bed). Homemade $Cu–ZnO–ZrO_2$ methanol catalytic system and a commercial H-ZSM5 zeolite were used to realize the hybrid system. The influence of preparation method on activity, selectivity and yield in the temperature range of 453–513 K at 3.0 MPa and $CO_2/H_2/N_2$ feed concentration of 3/9/1 has been evaluated. The results obtained under kinetic conditions show a superior specific productivity of *ca.* $430\,g_{total\,MeOH}\,kg_{cat}^{-1}\,h^{-1}$ at 513 K using the hybrid catalyst prepared by physical mixing. A combined effect of sites located at metal/oxide(s)-acid interface to drive DME synthesis through a consecutive mechanism was claimed as the main factor affecting the CO_2 conversion and DME productivity.

1. Introduction

CO_2 conversion into useful chemicals, like methanol and/or dimethyl ether (DME), is an attractive way to cut down the *greenhouse-gas* emissions, also accomplishing an effective recycle of carbon dioxide [1–5]. Currently, DME is proposed as an alternative clean fuel for diesel engines and household uses, also being a potential hydrogen carrier for fuel cells applications [5–7].

Notwithstanding an extensive literature documents the feasibility of a process for the production of DME *via* syngas [8–19], only few papers deal with the direct (one step) DME synthesis by CO_2 hydrogenation [5,20–29], even if many experiments performed at high contact time and approaching the equilibrium values do not allow to assess a "real" catalytic performance in a full kinetic regime [21,22,28,30–32].

Catalysts for the direct CO_2-to-DME process should be able to efficiently catalyze both the methanol synthesis and the methanol dehydration reactions. This can be accomplished by using bifunctional or hybrid catalysts, typically composed by a Cu–ZnO-based methanol synthesis catalyst [4,5] and a solid acid, like γ-Al_2O_3 [33–37] or H-ZSM5 zeolite [38–46].

Among several catalytic formulations proposed for methanol synthesis, according to previous studies, the $Cu–ZnO–ZrO_2$ (ZCZ) system [47–50], prepared by "*reverse co-precipitation under ultrasound irradiation*" of catalyst precursors had shown a superior activity compared to conventional catalysts. In particular, the role of metal/oxide(s) interface resulted to be crucial, owing to the interaction of metal Cu particles with both ZnO and ZrO_2 leading to the stabilization of $Cu^{\delta+}$ sites and a "mix" of Cu^0, $Cu^{\delta+}$ and oxide basic sites concurring to the adsorption/activation of H_2, CO and CO_2 [19,47–49].

Besides, as so far reported [34,44,51], H-ZSM5 is more suitable than γ-Al_2O_3 as the dehydration component in bifunctional/hybrid CO_2-to-DME catalysts as the former exhibits much higher activity at moderate reaction temperatures (*ca.* 473–533 K) which are thermodynamically more favourable for the methanol synthesis step [36,51]. Furthermore, water formed by CO_2 hydrogenation and methanol dehydration strongly adsorbs on the Lewis acid sites of γ-Al_2O_3 inhibiting DME formation. By contrast, the effect of water is much less significant for H-ZSM5 owing to its more hydrophobic character and predominance of Brønsted-type acidity [36,44,51]. Still, operation at moderate reaction temperature (<543 K) avoids the need for partially exchanging zeolite, as the inhibition of strong acid sites affecting coke and hydrocarbons formation is not necessary [36].

Therefore, the aim of this work is to investigate the behaviour of a hybrid system constituted by $Cu–ZnO–ZrO_2$ methanol synthesis catalyst [48–50] and a commercial H-ZSM5 zeolite. The influence of the procedure chosen for the combination of the two active phases on activity, selectivity and productivity of the catalytic system in the direct hydrogenation of CO_2–DME is discussed.

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2. Experimental

2.1. Catalyst preparation

Cu–ZnO–ZrO_2 methanol catalyst (ZCZ) was prepared by "reverse coprecipitation method under ultrasound irradiation", as elsewhere described [50].

A commercial NH_4-ZSM5 zeolite (*CBV 3024E*, Zeolyst International, SiO_2/Al_2O_3 = 30 mol/mol, SA_{BET} = 400 $m^2\,g^{-1}$) was converted in its protonic form (HZ30) by calcination at 773 K in static air for 5 h. All the samples were crushed and sieved and the 40–70 mesh particle size fraction was used for characterization and testing measurements.

Experiments were carried out by charging the reactor with a hybrid system "ZZ", prepared using different combination procedures, as following described:

(a) homogeneous physical mixture, constituted by two pre-pelletized ZCZ and HZ30 catalysts (ZZ-M);
(b) dual-bed composed by a pre-pelletized ZCZ methanol catalyst (first bed) and HZ30 catalyst (second bed) (ZZ-D);
(c) mono-bed constituted by a homogeneous solid mixture, prepared by grinding in an agate mortar of powdered single catalysts and pelletization of the resulting hybrid system (ZZ-G).

2.2. Catalysts characterization

2.2.1. Surface area (SA) and pore volume (PV)

SA and PV values of catalysts were determined from nitrogen adsorption/desorption isotherms at −196 °C, using a *Sorptomatic 1900 Instrument* gas adsorption device. The isotherms were elaborated according to the BET method for surface area calculation, while Horwarth–Kavazoe (HK) and Barrett–Joyner–Halenda (BJH) methods were used for micro- and meso-pores evaluation, respectively.

2.2.2. Temperature programmed reduction (TPR)

The measurements of reducibility in hydrogen atmosphere were performed in a linear quartz micro-reactor (i.d. 4 mm) fed with a 5 vol.% H_2/Ar purified carrier at the flow rate of 60 *STP* mL min^{-1}. The experiments were carried out in the range 273–1173 K with a heating rate of 20 K min^{-1}. The hydrogen consumption was monitored by a TCD, calibrated by the peak area of a known amount of CuO. TPR data resulted very reproducible both in maximum position (±3 K) and extent of H_2 consumption (±3%).

2.2.3. Transmission electron microscopy (TEM) analysis

TEM observations were made by using a *Philips CM12* instrument equipped with a high-resolution camera which allows acquisition and elaboration of the images. Specimens were prepared by ultrasonic dispersion of catalyst samples in isopropyl alcohol depositing a drop of suspension on holey carbon grid.

2.2.4. Ammonia temperature programmed desorption (NH_3-TPD)

NH_3-TPD measurements for the surface acidity determination were performed in a conventional flow apparatus by using 100 mg sample in a linear quartz micro-reactor (*internal diameter*, 4 mm; *length*, 200 mm), with a helium carrier flow rate of 25 *STP* mL min^{-1}. The experiments were carried out in the range 373–973 K with a heating rate of 10 K min^{-1}. The ammonia desorption was monitored by a thermal conductivity detector (TCD), calibrated by the peak area of known pulses of NH_3. Prior to each measurement, the sample was pretreated at 573 K with hydrogen flowing at 100 mL min^{-1} for 1 h and then cooled down to 423 K and saturated at a flow rate of 25 mL min^{-1} for 1.5 h with a 5% NH_3/He stream. Then, the samples were purged in He atmosphere for *ca.* 1 h until a constant TCD level was obtained.

2.3. Catalyst testing

The catalytic activity was investigated in a fixed-bed stainless steel reactor (*internal diameter*, 4 mm; *length*, 200 mm) at temperature ranging from 453 to 513 K and a total pressure of 3.0 MPa (*F* = 2.4 *STP* L/h; $CO_2/H_2/N_2$ = 3/9/1), using 0.25 g of hybrid catalyst (40–70 mesh), diluted with granular SiC (0.25 g). Prior to each test, the catalyst was reduced *in situ* at 573 K 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 detector* (FID) and *thermal conductivity detector* (TCD) respectively. Conversion values of CO_2 (X_{CO_2}) were calculated by both internal standard (a) and mass-balance (b) methods,

$$X_{CO_2} = 1 - \left[\left(\frac{CO_{2,out}}{CO_{2,in}}\right)\cdot\left(\frac{N_{2,in}}{N_{2,out}}\right)\right] \qquad (a)$$

and

$$X_{CO_2} = \frac{CO_{2,out}}{\Sigma_{Pi} + CO_{2,out}}, \qquad (b)$$

with product selectivity data (S_{Pi}) obtained from standard formulae:

$$S_{Pi} = \frac{P_i}{1 - CO_{2,out}} \qquad (a')$$

and

$$S_{Pi} = \frac{P_i}{\Sigma_{P_i}} \qquad (b')$$

where P_i stands for the concentration of a specific *i* product (*i.e.*, DME, MeOH, CO).

Each data set was obtained, with an accuracy of ±3%, from an average of three independent measurements.

3. Results and discussion

3.1. Textural properties

Table 1 shows the textural properties of the ZCZ and HZ30 components. The calcined ZCZ methanol synthesis catalyst displays a BET surface area of 173 $m^2\,g^{-1}$, which undergoes a significant shrinkage (*ca.* 54%) upon reduction treatment. Moreover, a decreasing pore volume before and after reduction (PV, 0.310–0.155 $cm^3\,g^{-1}$) mirrors a growth of the average pore diameter (APD) from 72 to 78 Å. On the other hand, typical BET and micropore volume values of 317 $m^2\,g^{-1}$ and 0.315 $cm^3\,g^{-1}$ were obtained for the HZ30 sample.

Being generally recognized that methanol forms directly from CO_2 and H_2 over a Cu single crystal with a very slow rate [52–54], the fundamental role of the metal/oxide interface, ensuring a suitable concentration of neighbouring hydrogenation and CO_2 activation sites, might be related to the promoting effect of both ZrO_2 and ZnO on the formation of the reaction intermediates *via* CO_2 adsorption [47–49]. Really, by an accurate TEM investigation of the reduced ZCZ system, it has been possible to discover that the core where the reaction occurs is mainly constituted by metallic copper Cu^0, decorated by Cu_2O, ZnO and ZrO_2, as clearly shown in Fig. 1, where the diffraction plane ⟨1 1 1⟩ corresponding to Cu_2O cuprite [JCPDS, 5-667], ⟨1 0 0⟩ relative to ZnO zincite syn hexagonal