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Research article

Direct synthesis of dimethyl ether from CO and CO_2 over a core-shell structured CuO-ZnO-ZrO_2@SAPO-11 catalyst

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ABSTRACT

The preparation by physical coating of a bifunctional core-shell-structured catalyst (CZZr@S-11), using CuO-ZnO-ZrO_2 (CZZr) as metallic function and SAPO-11 (S-11) as acid function, has been studied. The effects of calcination temperature and mass ratio between the metallic and acid functions (M/A) on their kinetic behavior for the synthesis of DME from syngas and CO_2 feeds has been assessed. The reaction indices considered have been: the conversion of CO_x ($CO + CO_2$) and CO_2; yields and selectivities of dimethyl ether (DME), methanol and hydrocarbons; and stability. The experiments have been carried out in a fixed-bed reactor (275 °C, 30 bar). The CZZr@S-11 catalyst prepared under suitable conditions (calcination at 400 °C and M/A of 1/2), shows better reaction indices than the hybrid catalyst (CZZr/S-11), prepared by physical mixture of the individual functions, which is explained by the advantages of the core-shell structure, especially interesting for the valorization of CO_2.

1. Introduction

The production of dimethyl ether (DME) has aroused a great attraction to meet the objectives of the energy sector, in order to produce ultra-clean fuels, reduce the dependence on oil and reduce CO_2 emissions. Thus, the properties of DME are suitable for its use as domestic and automotive fuel [1–3]; as H_2 vector by reforming [4,5] and as raw material for the production of olefins or aromatics [6,7].

DME can be obtained (via gasification and reforming) from fossil sources alternative to oil (coal, natural gas) and from lignocellulosic biomass or wastes of the consumer society (plastics, tires). In addition, the direct synthesis of DME, using bifunctional catalysts, is considered to be a suitable route for the large-scale valorization of CO_2, co-fed together with syngas [8]. The reactions involved in the direct synthesis of DME from syngas and CO_2 are:

Methanol synthesis:

$$CO + 2H_2 \leftrightarrow CH_3OH \tag{1}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{2}$$

Water gas shift (WGS):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

Methanol dehydration to DME:

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \tag{4}$$

Besides, undesired secondary reactions also take place, and methane, hydrocarbons (alkanes and light alkenes) and coke are formed through mechanisms catalyzed by the metallic sites (methanation, Fischer-Tropsch synthesis) and the acid sites (hydrocarbon pool mechanism, cracking) of the catalyst.

Carrying out the reaction of methanol dehydration (Eq. (4)), in the same reactor as the methanol synthesis reactions (Eqs. (1) and (2), and WGS, Eq. (3)), displaces the thermodynamic equilibrium of these latter reactions [9]. In addition, the lower thermodynamic limitation of the direct synthesis of DME favors the per-pass conversion of CO_2 compared to the synthesis of methanol [10] and to the two-stage process [11–13].

Among the initiatives to upgrade the production of DME and the conversion of CO_2, the studies aimed at using H_2O permeable membrane reactors [12,14–21], the integration of a CO_2 activation step by plasma [22] and the proposal of new bifunctional catalysts stand out.

The development of bifunctional catalysts for the direct synthesis of DME has received great attention in the literature [23]. As metallic function, conventionally, catalysts for the synthesis of methanol are used (CuO-ZnO-Al_2O_3), and the research has been focused on increasing their stability, improving the dispersion of Cu and incorporating different metallic promoters (Fe, Mg, Mn and Zr oxides) [24–26]. In this regard, the addition of ZrO_2 is effective for stabilizing $Cu^{\delta+}$ sites in a reaction medium with high water content, such as that corresponding to CO_2 hydrogenation [27–30]. In the CuO-Fe_2O_3-CeO_2 function, the

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presence of CeO_2 promotes CuO dispersion, increasing the conversion of CO_2, DME selectivity and the stability of the catalyst [31,32]. The most used acid function was initially γ-Al_2O_3 (catalyst used for the dehydration of methanol to DME in the two-stage process) [33]. However, due to its hydrophilicity and water adsorption capacity, the high selectivity to DME of the γ-Al_2O_3 results in a limited activity under the conditions of direct synthesis of DME. To overcome this drawback, different zeolites have also been used in the preparation of the bifunctional catalysts. In this regard, HZSM-5 zeolite (subjected to different modifications) [31,32,34] and silicoaluminophosphates (SAPOs), such as SAPO-18 [35] are to be highlighted. In the preparation of these materials, the acid strength of their sites must be limited, in order to minimize the formation of hydrocarbons from methanol and DME, since these reactions take place through the hydrocarbon pool mechanism, activated by the Brönsted sites [36].

Conventionally, hybrid catalysts are used, whose particles are prepared by physical mixture of the metallic and acid functions, and subsequent pelletizing. The incorporation of both functions in the same catalyst particle favors the synergy of the reactions catalyzed by each function. Bearing this objective in mind, in the recent years, the additional advantages of the core-shell structure have been explored [37]. This structure has been used in bifunctional catalysts for different reactions with complex reaction schemes (such as the Fischer-Tropsch synthesis), with the aim of reducing the thermodynamic limitations, as the individual reactions take place in different regions of the catalyst particle [38–40]. As to the direct synthesis of DME concerns, core-shell catalysts with different composition have been studied, such as CuO-ZnO-Al_2O_3@HZSM-5 [41,42], Cr-ZnO@HZSM-5 [43], HZSM-5@CuO-ZnO [44] or CuO-ZnO-Al_2O_3@SiO_2-Al_2O_3 [45]. Among the reasons of the better behavior of the core-shell catalysts compared to the hybrid catalysts, these works highlight the greater availability of the acid sites in the shell for the conversion of the methanol formed in the core, that diffuses towards the outside of the particle. A greater resistance to the sintering of Cu species in the core has also been observed. Furthermore, the core-shell structure allows minimizing adverse effects resulting from the interaction between the individual functions, which has been related to deactivation by various authors [44,46–51].

As an initiative to improve the formulation of core-shell catalysts, a physical coating method has been proposed by Pinkaew et al. [52] and by Phienluphon et al. [53] for the preparation of Cr-ZnO@SAPO-46 and CuO-ZnO-Al_2O_3/SAPO-11 catalysts, respectively.

In the present paper, the preparation stages and the properties of a core-shell catalyst prepared by physical coating, and its behavior (conversion, DME yield and selectivity, stability) in the direct synthesis of DME from syngas and CO_2 have been studied. In addition, the properties and catalytic behavior of the core-shell catalyst have been compared with those corresponding to hybrid catalysts, prepared by physical mixture of the same functions. For the study, CuO-ZnO-ZrO_2 has been used as metallic function. This function has been selected based on its good performance (activity, selectivity and stability) in the synthesis of methanol from CO_2 containing feeds [30]. As acid function, SAPO-11 has been used, whose behavior in the dehydration of methanol has been proven to be better than that of other functions such as SAPO-18 and HZSM-5 zeolites subjected to different treatments for the passivation of its acidity [54].

2. Experimental

2.1. Catalyst preparation

2.1.1. Metallic function

The CuO-ZnO-ZrO_2 metallic function for the synthesis of methanol (named CZZr hereafter) with 2:1:1 Cu:Zn:Zr atomic ratio, has been prepared following a conventional co-precipitation method [30,55–57]. It has been precipitated by drop-wise addition of an aqueous acid solution of Cu, Zn and Zr nitrates (1 M) and an aqueous basic solution of Na_2CO_3 (1 M), in deionized water, under stirring at 70 °C and pH range of 6.8–7.2. Then, the precipitated metallic function has been filtered, washed to remove Na^+ ions, and dried, at room temperature for 12 h and at 110 °C for another 12 h. Finally, the resultant dried powder has been calcined at 300 °C for 10 h.

2.1.2. Acid function

The acidic function, SAPO-11 (named S-11 hereafter), has been synthesized following the method based on a patent of the Union Carbide Corporation [58], using H_3PO_4 (85 wt%, Merck), Ludox AS-40 (Aldrich) and Disperal (Sasol) as P, Si and Al source, respectively, and dipropylamine (Aldrich) as organic template [54].

The crystallization has been carried out in a Teflon coated autoclave reactor (Highpreactor BR-300 from Berghof) at 195 °C for 24 h under constant stirring. Subsequently, the precipitate has been separated and washed to remove possible template remains from the interior of the pores. Finally, it has been dried, following the same sequence as with the metallic function, and has been calcined at 575 °C for 8 h.

2.1.3. Hybrid catalyst

The conventionally structured CZZr/S-11 catalyst, with homogeneous distribution of the metallic and acid functions over the particle, has been prepared by dry physical mixture (PM) of both functions (CZZr and S-11). The metallic and acid functions have been mixed in a mass ratio of 1/2, finely powdered, grinded and pelletized. Finally, the bifunctional catalyst has been crushed and sieved to the desired particle size (125–800 μm).

2.1.4. Core-shell catalyst

The core-shell-like catalyst (CZZr@S-11) is conformed by a metallic core coated by an acid shell, following the general methodology described in the literature [39,52,53]. First, the metallic function (CZZr) has been pelletized, crushed and sieved to 90–120 μm for the preparation of the cores. Subsequently, for the encapsulation, the metallic cores have been moistened in the adhesive solution, a diluted silica sol (Ludox TMA-34, Aldrich, 16% in deionized water). The moistened cores have been mixed with the acid function powder (S-11), in the desired metallic/acid mass ratio, in a round bottomed flask under vigorous movements until the complete adhesion of the total amount of acid function, obtaining relatively uniformly coated catalyst particles. The coated particles have been dried for 12 h at 110 °C and calcined to strengthen the shell. Finally, the catalyst particles have been sieved to the desired particle size (125–800 μm). In addition, aiming at studying the effect in the properties of the core-shell catalysts and its kinetic behavior, different calcination temperatures have been tested, 300–700 °C.

2.2. Catalyst characterization

The physical properties (BET specific surface area, micropore volume and total pore volume) of the individual functions and bifunctional catalysts have been determined by N_2 adsorption-desorption in a Micromeritics ASAP 2010 equipment. The experimental procedure consisted of degasification of the sample at 150 °C for 8 h under vacuum (10^{-3} mm Hg) for impurities removal, followed by N_2 adsorption-desorption in multiple equilibrium stages at −196 °C until the complete saturation of the sample.

Energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM), using a JEOL JSM-7000F instrument equipped with a W filament has been used for the characterization of the surface morphology. The chemical composition of the metallic functions, thus, Cu:Zn:Zr atomic ratio, has been determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES), in a Perkin Elmer Optima 8300 equipment. The procedure involves an acid attack of the sample with HNO_3 and H_2SO_4 (1:2 ratio) at 190 °C for 24 h in a closed teflon container; obtaining of a solid residue by evaporation of