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# Study of the interaction between components in hybrid CuZnAl/HZSM-5 catalysts and its impact in the syngas-to-DME reaction

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ABSTRACT

Hybrid CuZnAl(CZA)/HZSM-5 catalysts were prepared by three mixing methods in order to analyze the possible existence of interactions between components and their impact in the STD process, namely: (a) grinding of powders prior to pelletizing (grinding method), (b) slurrying the two solids in water followed by drying and pelletizing (slurry method), and (c) physical mixture of pre-pelletized components. The materials were characterized by ICP-OES, XRD, $N_2$ physisorption, $H_2$-TPR, $^{27}$Al MAS NMR, FTIR-pyridine, and EPR spectroscopy. Detrimental interactions producing a drastic reduction in the amount of available zeolitic Brønsted acid sites were observed for the hybrids prepared by slurry and grinding methods. Such interactions involved, on one hand, the partial blockage of micropores by CZA particles and, on the other hand, an inter-cationic exchange of $Cu^{2+}$ (and possibly also $Zn^{2+}$) species. The presence of isolated $Cu^{2+}$ cations occupying exchange positions in the HZSM-5 zeolite was unambiguously evidenced by EPR spectroscopy. The decrease in Brønsted acidity significantly reduced the activity of the zeolite for dehydrating methanol leading to a much lower efficiency of the corresponding hybrids for DME synthesis at typical STD conditions as compared to the catalyst obtained by simple mixture of pre-pelletized components.

## 1. Introduction

Dimethyl ether (DME) is an important intermediate for the production of useful chemicals (i.e. methyl acetate and dimethyl sulfate) and petrochemicals (light olefins, BTX aromatics) [1,2]. Recently, DME has also been considered as an ideal eco-friendly substitute for conventional petroleum-derived diesel owing to its high cetane number (55–60), low auto-ignition temperature, lower emissions of toxic compounds upon combustion, and reduced noise [3,4]. DME is traditionally produced by a two-step process involving first the synthesis of methanol from syngas on a Cu-based catalyst followed by the dehydration of methanol in the presence of a solid acid catalyst. Though the syngas feeding the methanol synthesis reactor is typically obtained from fossil resources such as coal, natural gas and crude oil, the production of DME from biomass-derived syngas (the so-called bioDME) is particularly attractive as in this case it can be considered as a carbon-neutral fuel from the viewpoint of $CO_2$ emissions thus contributing to restrain the global warming effect caused by the emission of greenhouse gases. The increasing interest in using DME (and particularly bioDME) as an environmentally benign diesel fuel has promoted extensive research in the so-called STD (syngas-to-DME) process in which DME is produced directly from syngas in a single catalytic reactor with the corresponding costs savings [5,6]. A salient advantage of the STD route is that, by rapidly consuming in situ the formed methanol, it allows overcoming the thermodynamic constraints of the methanol synthesis reaction allowing much higher per-pass CO conversions (and thus DME yields) to be attained as compared to the conventional two-step process. This can be easily inferred by looking to the main four reactions involved in the STD process described by the following Eqs. (1)–(4):

$$2CO + 4H_2 \leftrightarrow 2CH_3OH \quad (1)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad (2)$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (3)$$

$$H_2O + CO \leftrightarrow H_2 + CO_2 \quad (4)$$

According to this set of reactions the product of one reaction is the reactant for another thus creating a synergistic effect that shifts the equilibrium of the methanol synthesis reactions (1) and (2) to the right.

It is clear from the above set of reactions that a suitable STD catalyst should combine two catalytic functionalities in order to effectively couple the methanol synthesis and methanol dehydration reactions. Typically, the methanol synthesis function is provided by a Cu-based catalyst (e.g. $CuO/ZnO/Al_2O_3$, abbreviated as CuZnAl) while the dehydration of methanol to DME is afforded by a solid acid component such as $\gamma$-$Al_2O_3$ or zeolites [7–12]. Among

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the zeolites, most of the studies were focused on the medium-pore HZSM-5 [7–9,12,13] as the size of its pores prevents extensive coking without severely hindering the diffusion of the molecules involved in the DME synthesis, although other zeolitic structures such as ferrierite [14,15], mordenite [13], and HY [10,15], as well as SAPO-*x* zeotypes [16] have also been explored. In general, zeolites are preferred over alumina since the much higher dehydration activity of the former (owing to a substantially higher acidity) allows for performing the STD reaction at lower temperatures and thus under thermodynamically more favorable conditions for the methanol synthesis step. Higher reaction temperatures do also tend to favor secondary reactions leading to hydrocarbons in detriment of DME and to carbon deposits that negatively impact the catalyst lifetime.

In order to attain a good synergy between the main reactions involved in the STD process and thus to maximize the DME formation rate, it seems reasonable *a priori* that the preparation of the bifunctional STD catalyst should target a close proximity between the active sites of the two catalytic functions as, in fact, it has been predicted in a reactor simulation study [17]. However, while being conceptually correct, earlier studies have clearly shown that the employment of preparation methodologies favoring a closer contact between components in hybrid CuO/ZnO/$\gamma$-$Al_2O_3$ catalysts (where $\gamma$-$Al_2O_3$ provides the methanol dehydration function) does not necessarily produce the most efficient STD catalysts [10,11,18]. A similar conclusion was drawn for CuZnAl/$SiO_2$–$Al_2O_3$ catalysts prepared using different strategies leading to different degrees of intimacy between components [19]. It is learned from these studies that the use of preparation methods, such as coprecipitation–impregnation, coprecipitation–sedimentation, sol–gel impregnation, or the simplest (and most widely applied) physical mixture of the two components, in where the active sites for the methanol synthesis and methanol dehydration functions are formed in separated stages, leads to more effective hybrid catalysts than when the active sites are generated from a common Cu–Zn–Al coprecipitate, even if the last approach is that conducting to a more intimate contact between components. This behavior may be accounted for by considering the existence of detrimental interactions between the two catalytic functions in intimate contact worsening the overall STD performance. Detrimental interactions between the methanol synthesis and dehydration functions may not only take place at the catalyst preparation and/or activation stages, as it is inferred from the above examples, but also they have been shown to occur during the liquid phase DME synthesis in slurry-type reactors (LPDME process) [20]. In this later case, based on SEM–EDS analyses of a spent CuO/ZnO/$\gamma$-$Al_2O_3$ hybrid catalyst prepared by physical mixture of the individual component powders, the interaction was suggested to occur by the migration of Cu- and Zn-containing species from the methanol catalyst to the alumina poisoning the acid sites active for methanol dehydration [20]. Nevertheless, due to the poor signal-to-noise ratio in the SEM–EDS measurements, a definitive conclusion regarding the *inter-catalyst migration* hypothesis as the likely interaction mechanism could not be made [20].

As mentioned previously, the most extended methodology for preparing hybrid STD catalysts, particularly for those comprising zeolites as the dehydration function, is the simple physical mixture of the individual components. In fact, a significant blockage of the zeolite micropores by the methanol synthesis component has been observed in hybrid Cu–Zn(–Al)/H-ferrierite catalysts prepared by coprecipitation–impregnation or coprecipitation–sedimentation methods [21,22]. However, even for catalysts prepared by physical mixture, it appears that detrimental interactions might also occur depending on the specific mixing method employed. For instance, Takeguchi et al. [23] reported that a Cu–Zn–Ga/silica–alumina catalyst prepared by mixing the previously pelletized components is more active for the syngas-to-DME reaction than the equivalent catalyst obtained by milling (grinding) the two component powders prior to pelletizing. The authors attributed this fact to the masking of active sites in the methanol synthesis component by the silica–alumina particles at the mixing and tabletting stages of the grinding approach, though no experimental proofs other than the different catalytic behaviors were presented.

Despite the above discussions clearly highlight the importance of the possible existence of detrimental interactions between components in hybrid STD catalysts (even in those prepared by the most common physical mixture approach) no much effort has been devoted in the previous literature to this issue. To the best of our knowledge, there are no previous studies aimed at addressing interaction effects in hybrid STD catalysts comprising zeolites as the dehydration component. In the present work we provide, for the first time, experimental evidences based on EPR characterization that such detrimental interactions may take place in hybrid CuZnAl/HZSM-5 catalysts depending on the mixing method used. The consequences of such interactions on the activity of the two catalytic functions are also addressed.

## 2. Experimental

### 2.1. Preparation of catalysts

A CuO–ZnO–$Al_2O_3$ methanol synthesis catalyst precursor with a nominal Cu:Zn:Al atomic ratio of 6:3:1 was prepared by coprecipitation following the optimized procedure reported in [24]. Specifically, an aqueous solution containing the respective metal nitrates [$Cu(NO_3)_2$ (0.6 M), $Zn(NO_3)_2$ (0.3 M), and $Al(NO_3)_3$ (0.1 M)] and an aqueous solution of $Na_2CO_3$ (1 M) as precipitating agent were simultaneously added at a rate of 5 mL/min to a glass beaker kept under stirring at 70 °C and a constant pH of 7.0. After the addition was completed, the suspension was aged for 1 h at the above conditions and the resulting precipitate was then filtered, exhaustively washed with deionized water, dried at 100 °C for 12 h, and finally calcined under a flow of air (25 mL/min) at 300 °C for 3 h. The methanol synthesis precursor so obtained is denoted here as CZA.

A commercial ZSM-5 zeolite (CBV8020, Zeolyst International, nominal Si/Al = 40) in its protonic form (sample denoted here as HZ) was used as the methanol dehydration function. Then, three different mixing methods were adopted in order to prepare the hybrid CZA/HZ samples: (a) addition of dry powders of the two components to a beaker containing deionized water at ambient temperature and stirring of the slurry for 30 min, followed by separation of the solid mixture by filtration, drying at 100 °C overnight, and pelletizing (hereinafter denoted as slurry method); (b) careful grinding of the individual component powders in an agate mortar for 15 min followed by pelletizing of the formed homogeneous solid mixture (denoted here as grinding method); and (c) simple physical mixture of the two pre-pelletized components. In all cases, catalysts pellets of 0.25–0.42 mm were used for the catalytic studies. Using the above three methods a series of hybrid CZA:HZ catalysts with variable mass ratios between components were produced for different characterization and catalytic purposes, as will be explained along the work. The hybrid catalysts were designated as CZA/HZ(*x*)Y, where *x* is the CZA:HZ mass ratio and Y is S, G, or M and refers to the mixing method used, i.e. S = slurry, G = grinding, and M = mixture of pellets.

In order to address how the mixing method applied affected the activity of the CZA component for the synthesis of methanol from syngas, mixtures of CZA with silicalite-1 (the pure silica MFI counterpart, abbreviated as S1) were prepared in a CZA:S1 mass ratio of 2:1 by the same three methods used for producing the CZA/HZ hybrids. The CZA/S1 mixtures were denoted as CZA/S1(2:1)Y (Y = S,