Direct synthesis of DME from syngas on hybrid CuZnAl/ZSM-5 catalysts: New insights into the role of zeolite acidity

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ABSTRACT

A commercial HZSM-5 zeolite (Si/Al = 16) was submitted to mild acid treatment and partial exchange of H^+ by Na^+ and Co^{2+} cations in order to produce samples with different amounts and strengths of Brønsted and Lewis acid sites. The acid properties of the zeolites were determined by both FTIR of adsorbed pyridine and NH_3-TPD. Then, hybrid catalysts comprising a $CuO/ZnO/Al_2O_3$ (CZA) methanol synthesis catalyst and the original and treated zeolites were prepared in order to analyze the impact of the zeolite acidity in the efficiency of the hybrids for the direct syngas-to-DME process. Independent methanol dehydration experiments on the bare zeolites and syngas-to-DME runs under methanol dehydration-controlled conditions were performed using hybrids with low zeolite concentration (CZA:zeolite mass ratio of 10:1) prepared by mixing the pre-pelletized CZA and zeolite components. The results revealed that both strong Brønsted and EFAL-related strong Lewis acid sites are the likely zeolite active sites for methanol dehydration at the typical syngas-to-DME temperature of 260 °C. Interestingly, we have found that different conclusions regarding the effect of zeolite acidity may be reached depending on the specific method used for preparing the hybrid catalysts when the overall syngas-to-DME process becomes controlled by the methanol synthesis rate on the Cu-based catalyst (i.e. using hybrids with a CZA:zeolite mass ratio of 2:1, that is, with an "excess" of acid sites). Thus, for hybrids prepared by mixing the pre-pelletized components, the same CO conversion and product selectivity (with values approaching those predicted by the thermodynamic equilibrium at the studied conditions) with no signs of deactivation during at least 50 h on stream was attained irrespective of the zeolite acidity. By contrast, significant differences in catalyst stability were found for hybrids prepared by grinding the component powders prior to pelletizing. This fact points towards the occurrence of detrimental interactions between the CZA and zeolite components during the grinding preparation stage. The kind and extent of such detrimental interactions are tightly related to the properties (i.e. acidity, chemical composition) of the ZSM-5 zeolite.

1. Introduction

Dimethyl ether (DME) is a well-known building block in the production of valuable chemicals such as methyl acetate and dimethyl sulfate, as well as of petrochemicals (BTX aromatics and light olefins) and conventional fuels by replacing methanol as raw material. Moreover, DME is attracting increasing interest as a potential eco-friendly substitute for petroleum-derived diesel fuel given its high cetane number (55–60), low auto-ignition temperature, and reduced emissions of hazardous compounds such as NO_x, SO_x, and particulate matter [1,2]. DME has also great potential as energy carrier, for instance, as a residential fuel for heating and cooking replacing LPG (liquefied petroleum gas), as fuel for power generation using DME-fired turbines, or as a source of hydrogen for fuel

cells applications [1]. Moreover, having physical properties similar to LPG, supply of DME to the end users could be well accomplished using the existing LPG infrastructure with minor investment costs.

Traditionally, DME is produced by a two-step process involving the conversion of syngas to methanol in the presence of a Cu-ZnO-based catalyst and its subsequent dehydration to DME on a solid acid catalyst [3]. Though typically syngas used in the methanol synthesis step is produced from fossil resources (natural gas, coal, and oil), the utilization of syngas derived from biomass via gasification has recently attracted considerable interest [4]. In the conventional process, the conversion of syngas to methanol is limited by the thermodynamic equilibrium requiring high pressures and low temperatures in order to attain reasonable per-pass conversions. Lately, a new one-step process for the direct conversion of syngas to DME has received much attention as it is thermodynamically and economically more advantageous than the traditional two-step technology [5,6]. The key reactions in the direct DME synthesis are the hydrogenation of CO and CO_2 (typically present in

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biomass-derived syngas) to methanol, the methanol dehydration to DME, and the water–gas-shift reaction (WGSR) according to the chemical equations (1)–(4) below:

$$2CO + 4H_2 \leftrightarrow 2CH_3OH \tag{1}$$

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

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \tag{3}$$

$$H_2O + CO \leftrightarrow H_2 + CO_2 \tag{4}$$

The concerted action of this set of reactions leads to a synergetic effect by which the methanol formed from CO/CO_2 hydrogenation is consumed through reaction (3) shifting the chemical equilibrium for the methanol synthesis reactions (1) and (2) to the right-hand side allowing high per-pass CO conversions to be attained. Moreover, the water formed in reactions (2) and (3) reacts with CO through the WGSR to produce CO_2 and H_2 (Eq. (4)), which are reactants for the methanol synthesis. It is clear, thus, that catalysts employed in the syngas-to-DME process should be able to efficiently catalyze both the methanol synthesis and the methanol dehydration reactions. This can be accomplished by using dual-function composite or hybrid catalysts typically comprising a Cu-ZnO-based methanol synthesis catalyst and a solid acid, most often γ-Al_2O_3 [7–11] or HZSM-5 zeolite [12–18], as the dehydration function. It is generally admitted that HZSM-5 is more suitable than γ-Al_2O_3 as the dehydration component in bifunctional syngas-to-DME catalysts as the former exhibits much higher activity at moderate reaction temperatures (ca. 240–280 °C) which are thermodynamically more favorable for the methanol synthesis step [9,19]. Furthermore, water formed by methanol dehydration (and CO_2 hydrogenation if present in the feed) 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 HZSM-5 owing to its more hydrophobic character and predominance of Brønsted-type acidity [9,14,19].

Since the methanol synthesis over Cu-type catalysts is a well established and quite optimized technology, much of the efforts in the research concerning the direct DME synthesis have been devoted to the study of the methanol dehydration function. The general conclusion one may withdraw from these previous studies is that the acid property of the dehydration component plays a crucial role in determining the overall CO conversion rate, DME selectivity, and catalyst durability. Therefore, a deep understanding of the role of the different types of acid sites (either Brønsted or Lewis) present in the dehydration catalyst, their amount, and strength becomes essential in order to perform the syngas-to-DME process in the most efficient way. Unfortunately, the previous literature in this respect is somehow unclear. This is likely due to the higher complexity of the syngas-to-DME process and catalyst composition with respect to the simpler methanol dehydration system which has led, in fact, to some contradictory or ambiguous conclusions. In many occasions it is observed that when the dehydration function is composed by strong solid acids, such as H-zeolites (particularly those with lower Si/Al ratio) or sulfated-zirconia, the overall syngas-to-DME reaction becomes controlled by the methanol synthesis step leading to a lack of correlation between the acidity of the dehydration catalyst and the catalytic performance [10,13,15,17,18,20–22]. In this situation the methanol formed on the Cu-based catalyst is rapidly consumed by the dehydration catalyst yielding a product composition close to that predicted by the equilibrium concentration at the employed syngas-to-DME conditions. Moreover, even under conditions where the direct DME synthesis is controlled by the methanol synthesis, discrepancies can also be found in the literature regarding the influence of acidity on the CO conversion or product selectivity. For instance, while Mao et al. [18] postulated that under these conditions the acidity

only influences DME selectivity without affecting CO conversion, Wang et al. [17] observed that increasing the amount of acid sites in the hybrid catalyst produced a decrease in CO conversion with no appreciable changes in DME selectivity. On the other hand, changes in both CO conversion and DME selectivity were noticed by the group of Hou when the acidity of HY zeolite (as dehydration component) was modified via ion-exchange with transitional [23] and rare earth [24] metals. In contrast to the above investigations, other authors did not find significant changes in CO conversion and DME selectivity with the acidity of the dehydration catalyst when the overall syngas-to-DME process is governed by the methanol synthesis step [13,20].

A lack of consensus is also evidenced from the previous literature on the direct DME synthesis with regards to the requirements in terms of type of acid sites and acid strength to effectively produce DME. As to the nature of the acid sites (a mechanistic discussion is out of the scope of the present work), Sarkadi-Priboczki et al. [25] and Takeguchi et al. [9] concluded that Lewis acid-base pairs are the major active sites for the methanol-to-DME reaction, whereas strong Brønsted acid sites (as those typically present in zeolites) favor the undesired conversion of DME to hydrocarbons. By contrast, Xia et al. suggested that extralattice Al species, which are typically associated to the development of Lewis-type acidity in zeolites, do promote the formation of hydrocarbons during the syngas-to-DME reaction [21]. In preceding studies, however, evidences were presented that Lewis acid sites in HZSM-5 are at the origin of catalytic activity in the conversion of methanol to DME [26]. By studying the effect of water addition on the methanol dehydration activity over different solid acids, Xu et al. concluded that both Brønsted and Lewis acid sites in HZSM-5 are active for DME formation [19]. Mao et al., on the other hand, did not find a direct relationship between the activity for methanol dehydration and the nature of the acid sites on HZSM-5 modified by basic MgO species and proposed a mechanism for DME formation involving both acidic and basic sites [18]. Quite often the contribution of different type of acid sites could not be assessed simply because the acidity of the dehydration catalysts was exclusively characterized by using the NH_3-TPD technique [10,13,15,17] which, obviously, is not able to discriminate between Brønsted and Lewis acid sites. Concerning the acid strength, many authors concluded (mostly based on NH_3-TPD profiles) that acid sites of intermediate (or moderate) strength are the most desirable from the viewpoint of DME selectivity, while strong acid sites do promote the formation of by-products at the expense of DME [9,10,19]. Others, however, stated that acid sites of relatively weak strength (again based on NH_3-TPD results) can also efficiently convert methanol to DME [18] or even that weak acid sites are more effective for the selective DME synthesis [12,27]. Just on the opposite side, Kim et al. [13] associated the dehydration activity of Na- and H-ZSM-5 samples to the presence of very strong acid sites characterized by NH_3 desorption temperatures above 500 °C (so-called γ sites).

It is apparent from the above discussions that more systematic work is required in order to gain more insights into the influence of the acid property of the dehydration catalyst, hopefully differentiating by type of acid site, density, and strength, on the activity and selectivity during the syngas-to-DME process. For this purpose, in the present investigation we have prepared a series of hybrid CuZnAl/ZSM-5 catalysts in which the zeolite acidity was systematically varied by submitting a commercial HZSM-5 sample to different post-synthesis treatments. The acid properties of the zeolite samples have been measured by applying both NH_3-TPD and FTIR-pyridine techniques. The catalytic behavior for the syngas-to-DME reaction of the prepared CuZnAl/ZSM-5 hybrids was determined under conditions where the overall reaction is either controlled by the methanol dehydration step (as confirmed