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Shoujie Ren

Shiguang Li

Naomi Klinghoffer

Miao Yu

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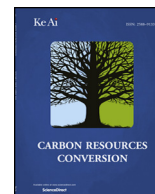Part of the Chemical Engineering Commons

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Effects of mixing methods of bifunctional catalysts on catalyst stability of DME synthesis via CO_2 hydrogenation

Shoujie Ren[a], Shiguang Li[b], Naomi Klinghoffer[b], Miao Yu[c], Xinhua Liang[a],*

[a] Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO 65409, United States
[b] Gas Technology Institute, 1700 South Mount Prospect Road, Des Plaines, IL 60018, United States
[c] Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States

HIGHLIGHTS

- Mixing method of catalysts significantly influenced catalyst stability.
- Mixing of pelletized catalysts had better stability.
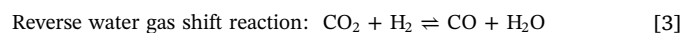- Mixing of pelletized catalysts reduced Cu oxidation.

ARTICLE INFO

ABSTRACT

The effects of three different mixing methods of $CuO/ZnO/Al_2O_3$ (CZA) and HZSM-5 bifunctional catalyst on the stability for dimethyl ether (DME) synthesis from carbon dioxide (CO_2) hydrogenation were investigated. When the bifunctional catalyst was prepared by method A (mixing powder without pelletization), there was no significant change in DME production and catalyst stability when the HZSM-5 loading was varied between 0.1 g and 0.5 g with a fixed CZA loading of 0.5 g,. When the bifunctional catalysts were prepared by method B (pressed into pellets of CZA and pellets of HZSM-5 and then mixed) and method C (mixed CZA and HZSM-5 powders, then pressed into pellets), the mixing methods did not initially impact CO_2 conversion and had a minor effect on DME yield. However, long-term tests (100 h) indicated that the mixing method had a significant influence on the catalyst stability. Method B showed the best stability and the extent of catalyst deactivation followed the sequence of method B < method A < method C. Characterizations of spent catalysts indicated that method B could reduce the extent of copper (Cu) oxidation, which due to the relatively low surface contact between Cu active sites and HZSM-5. Large amounts of water generated in CO_2 hydrogenation to synthesize DME and intimate contact between CZA and HZSM-5 catalyst could induce severe oxidation of Cu and metal ions migration from hydrogenation catalyst to HZSM-5, which can result in the number reduction of acidic sites.

1. Introduction

The utilization of carbon dioxide (CO_2) to produce value-added chemicals and fuels has attracted great interest as it can help control greenhouse gas emissions [1–5]. Dimethyl ether (DME) as the simplest ether has a high cetane number of 55, low emission of nitrogen oxide (NO_x) and carbon monoxide (CO), and it is easily liquefied at low pressure. DME has been considered as a promising alternative fuel for diesel engines [6]. DME can be directly synthesized via CO_2 hydrogenation to form methanol followed by methanol dehydration using bifunctional catalysts. The process involves three major reactions, including the reverse water gas shift as a side reaction [7,8]:

$$CO_2 \text{ hydrogenation to methanol: } CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad [1]$$

$$\text{Methanol dehydration to DME: } 2CH_3OH \rightleftharpoons DME + H_2O \qquad [2]$$

$$\text{Reverse water gas shift reaction: } CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad [3]$$

Different hydrogenation catalysts for CO_2 conversion to methanol including copper-zinc oxide- based (Cu-ZnO-based) catalysts [9–12], palladium-based (Pd-based) catalysts [13–15], and bimetallic catalysts [6,16,17] have been investigated. Among these catalysts, CuO-ZnO-Al_2O_3 (CZA) catalysts have shown high activity, and multiple preparation methods have been developed. Previous studies have proven that the activity of the catalyst was significantly affected by catalyst

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* Corresponding author.
  E-mail address: liangxin@mst.edu (X. Liang).

preparation conditions and high activity could be achieved by precise control of preparation parameters, such as initiation temperature, pH value, washing, and aging time [6,18]. Some catalyst properties, such as high surface area and number of active Cu sites, which contribute to high activity of Cu-ZnO-based catalysts, can be achieved by conventional methods, such as co-precipitation [19,20]. Due to its high activity and easy preparation, Cu-ZnO-based catalysts have been used with solid acid catalysts, such as HZSM-5 and γ-Al$_2$O$_3$ to prepare bifunctional catalyst, for directly converting CO$_2$ to DME [21–25]. In previous studies, multiple preparation methods of bifunctional catalysts, which included physical mixing, mechanical mixing, impregnation, and co-precipitation, have been investigated [7,23,26–28]. Reducing catalyst deactivation is critical for enabling the use of this catalyst in commercial processes. The major causes of deactivation in this process are coking and Cu sintering, which have been observed with this bifunctional catalyst [8,12,23,29]. Recent studies found that the presence of water in the feed or formed during the reaction attenuated the coking formation for both the hydrogenation and dehydration catalysts [24,25,30]. However, the presence of water would weaken the activity of the hydrogenation catalyst and the acidity of dehydration catalyst, and thus lead to the reduction of CO$_2$ conversion and DME production [21,24,28]. Frusteri et al. studied the catalytic behavior of a copper-zinc-zirconium/zeolite (Cu-Zn-Zr/zeolite) hybrid catalyst system prepared by co-precipitation of metal precursors in a slurry of zeolites [28]. The hybrid catalyst enhanced the interaction of metal oxides and active sites, and improved the mass transfer of methanol from the metal oxide site to the solid acid site of the zeolite, thereby improving the DME productivity; however, they also observed a progressive loss of activity during the first 15 h of reaction. This phenomenon was mainly attributed to the water formed during reaction, which blocked the active sites via an occupation of oxygen vacancies (which are responsible for CO$_2$ activation) and weakened activity for methanol formation. Therefore, developing a proper preparation method for a bifunctional catalyst in order to reduce or eliminate the effects of water formed in reaction is important not only for the catalytic activity but also for the catalyst stability.

In our previous work, we developed a highly active and selective CuO/ZnO/Al$_2$O$_3$ (CZA) catalyst for direct conversion of CO$_2$ to DME [31]. Similar to Frusteri's observation during a stability test, CO$_2$ conversion and DME selectivity of our bifunctional catalyst (prepared by physically mixing powders of CZA and HZSM-5) reduced quickly at the first 20–30 h. In addition to the coking and Cu sintering, a migration of metal ions from hydrogenation catalyst to dehydration catalyst have been identified in the hybrid catalysts for syngas to DME synthesis [32–38]. Compared to DME synthesis from syngas (where DME is formed primarily from the reaction of CO and H$_2$), the reverse water gas shift reaction is more significant in our process due to CO$_2$ being one of the primary reactants. In addition, more water is generated, which could enhance the hydrothermal sintering of Cu and the migration of metal ions from hydrogenation catalyst to dehydration catalyst thereby reducing the number of metal active sites and blocking acidic sites [21,28].

Previous studies have shown that surface contact patterns between hydrogenation and dehydration catalysts can be formed by using different mixing methods and these surface contact patterns affected the catalyst activity and stability in syngas hydrogenation to DME [33,35]. Although the effects of different mixing methods on catalytic activity of CO$_2$ hydrogenation to DME have been investigated [7,26], there are few reports focusing on the stability of bifunctional catalysts. Therefore, the main objective of this study is to investigate the effects of catalyst mixing methods on the catalyst stability during CO$_2$ hydrogenation to synthesize DME. To form different surface contact patterns, three mixing methods were used for preparing bifunctional catalysts: unpressed bifunctional catalyst (mixed by powders, method A), pressed then mixed (method B), and mixed then pressed (method C). The effects of mixing methods on the catalytic performance of DME synthesis were

investigated. Different HZSM-5 loadings in bifunctional catalysts were also evaluated. Long-term tests of the bifunctional catalysts prepared using these three methods were performed to evaluate their catalytic behavior and stability.

2. Experimental

2.1. Materials

The CuO/ZnO/Al$_2$O$_3$ hydrogenation catalyst was synthesized using copper nitrate (Cu(NO$_3$)$_2$·3H$_2$O, 99%), zinc nitrate (Zn(NO$_3$)$_2$·6H$_2$O, 98%), aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O, 98%), and sodium carbonate (Na$_2$CO$_3$, 99%). HZSM-5 was used as a dehydration catalyst. HZSM-5 was obtained by calcining of ammonia-ZSM-5 (surface area: 438 m^2/g, particle size: 5.8 μm) at 500 °C for 5 h. All the chemicals and ammonia-ZSM-5 were purchased from Alfa Aesar (Wardhill, MA, USA). A pre-mixed gas (25 mol.% carbon dioxide and 75 mol.% hydrogen) purchased from Airgas Inc. (Chicago, IL, USA) was used for the reaction.

2.2. CuO/ZnO/Al$_2$O$_3$ catalyst synthesis and bifunctional catalyst preparation

The CuO/ZnO/Al$_2$O$_3$ catalyst with an atomic ratio of Cu:Zn:Al = 6:3:1 was prepared using a co-precipitation method presented in our previous study [31]. Briefly, a 0.1 M mixed aqueous nitrate solution (copper nitrate, zinc nitrate, and aluminum nitrate) and a 0.1 M aqueous sodium carbonate solution were simultaneously added dropwise into 400 mL of preheated deionized (DI) water under vigorous stirring. The temperature of co-precipitation was kept at 65–70 °C and pH value was at 6.5–7.0. After co-precipitation, the precipitates were aged for 30 minutes at 70 °C under stirring. Then the precipitates were filtered and washed with warm DI water. The washed precipitates were dried in an oven at 110 °C overnight and calcined at 360 °C for 4 h with a heating rate of 2 °C/min.

To determine the effects of mixing method on the DME synthesis, three different mixing methods were used to produce a bifunctional catalyst:

Method A: Physically mix catalyst powders. The particle size of CZA after grinding and calcination was less than 80 mesh (< 177 μm) and the particle size of HZSM-5 was 5.8 μm. The HZSM-5 catalyst (with loading ranging from 0.05 g to 0.5 g) was physically mixed with 0.5 g of calcined CZA.

Method B: Pressed then mixed. The calcined CZA and HZSM-5 were first pressed using a Carver Press (Model C, Carver Inc., Wabash, IN, USA), crushed, and sieved to get 40–60 mesh particle size separately, and then the CZA (0.5 g) and HZSM-5 (0.1 g to 0.5 g) catalysts with the same particle size (40–60 mesh) were mixed homogeneously to form a bifunctional catalyst for the experiments.

Method C: Mixed then pressed. The calcined CZA powder fixed at 0.5 g was first physically mixed with an appropriate amount (0.1 g to 0.5 g) of HZSM-5. The mixed bifunctional catalyst was then pressed, crushed, and sieved to get 40–60 mesh particle size for the experiments.

2.3. Catalyst characterization

A Quantachrome Autosorb-1 (Quantachrome Instruments Inc., Boynton Beach, FL, USA) was used for nitrogen (N$_2$) adsorption and desorption at −196 °C to determine the surface area (SA) of catalysts. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method in a relative pressure range of 0.05–0.25.

N$_2$O-chemisorption was used to determine the metallic Cu surface area, Cu dispersion, and Cu crystalline size [10]. The N$_2$O-chemisorption analysis was performed by using a Micromeritics AutochemII 2920 (Micromeritics Instrument Corp., Norcross, GA, USA). Fresh and spent catalysts were first degassed at 250 °C for 2 h with pure helium (He), then reduced in 10% hydrogen (H$_2$) in He for 2 h at the same
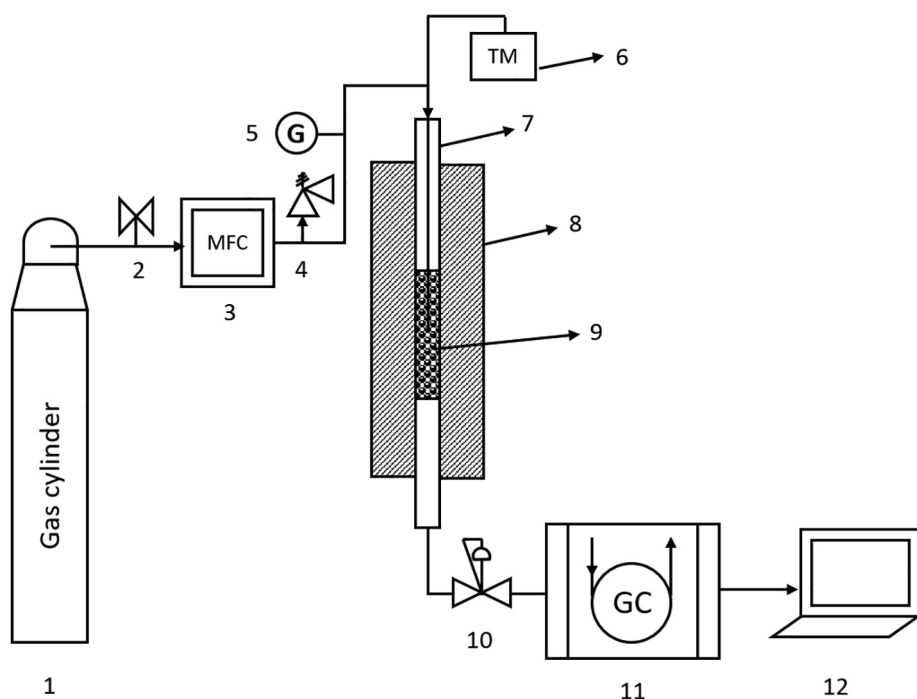
Fig. 1. Schematic diagram of reaction system for DME synthesis from CO_2 hydrogenation with bifunctional catalysts. 1. Premixed gas of H_2 and CO_2 (H_2/CO_2 = 3:1), 2. Valve, 3. Mass flow controller, 4. Pressure relief valve, 5. Pressure gauge, 6. Thermometer, 7. Tubular reactor, 8. Furnace, 9. Bifunctional catalyst, 10. Back pressure regulator, 11. Gas chromatography, 12. Data collector.

temperature. After reduction, the sample was purged with He to cool down to 50 °C. Then, the gas was switched to a mixture of 1% N_2O in He to start N_2O-chemisorption. The stoichiometry of Cu:N_2O was assumed to be 2:1.

Powder X-ray diffraction (XRD) patterns were obtained by a PANalytical X'Pert MultiPurpose Diffractometer (Malvern Panalytical Ltd, Westborough, MA, USA) equipped with a Cu Kα radiation and a graphite generator. The tube voltage and the current were at 45 kV and 40 mA, respectively. The scan range was 20–90° with a scan rate at $0.5° \, min^{-1}$.

The coking amount in the spent catalysts was analyzed by a TA Instruments SDT Q600 thermogravimetric (TG) analyzer (New Castle, DE, USA). The spent catalysts were first heated to 100 °C, at a heating rate of 10 °C/min, and kept at 100 °C for 60 min with N_2 (100 mL/min) to remove any moisture and adsorbed CO_2. Then the catalyst was heated to 1000 °C at the same heating rate with air (100 mL/min).

2.4. Catalytic testing of DME synthesis

Catalyst testing was performed in a fixed-bed stainless steel reactor (I.D. = 9.525 mm) system, as schematically shown in Fig. 1. A certain amount of bifunctional catalyst (CZA fixed at 0.5 g, HZSM-5 varied from 0.05 g to 0.5 g depending on reactions) prepared by different mixing methods was loaded into the reactor for DME synthesis. The reduction for the bifunctional catalyst was performed at 250 °C for 10 h with 20 sccm of pure H_2. The DME synthesis was carried out with 18 sccm of H_2 and 6 sccm of CO_2 at reaction temperatures of 220–280 °C, and pressure of 400 psig. Gas hourly space velocity (GHSV) was at 1525–2773 NL/(kg·h) depending on the amount of catalyst loading. After the pressure and temperature of the reaction system was stabilized for about 1 hour, the products were analyzed by an on-line gas chromatograph (GC, model: SRI 8610C, SRI Instruments, Torrance, CA, USA) equipped with a 6-foot HAYESEP D column, a 6-foot molecular sieve 13X column, and a thermal conductivity detector (TCD). The GC was programed at 50 °C for 4 min, then increased to 180 °C at 40 °C/min and held for 5 min. The flowrate of carrier gas (He) was 30 mL/min. For each reaction temperature, after reaction was stable, six sampling points were analyzed and the average data were reported.

The CO_2 conversion (X_{CO_2}), product selectivity (S_{CO}, $S_{Methanol}$, and S_{DME}), and yield (Y_{CO}, $Y_{Methanol}$, and Y_{DME}) were calculated as follows [31]:

$$X_{CO_2} = \frac{nCO + nMethanol + 2nDME}{nCO_2 + nCO + nMethanol + 2nDME} \times 100\% \qquad [4]$$

$$S_{CO} = \frac{nCO}{nCO + nMethanol + 2nDME} \times 100\% \qquad [5]$$

$$S_{Methanol} = \frac{nMethanol}{nCO + nMethanol + 2nDME} \times 100\% \qquad [6]$$

$$S_{DME} = \frac{2nDME}{nCO + nMethanol + 2nDME} \times 100\% \qquad [7]$$

$$Y_{CO} = \frac{nCO}{nCO_2 + nCO + nMethanol + 2nDME} \times 100 \qquad [8]$$

$$Y_{Methanol} = \frac{nMethanol}{nCO_2 + nCO + nMethanol + 2nDME} \times 100 \qquad [9]$$

$$Y_{DME} = \frac{2nDME}{nCO_2 + nCO + nMethanol + 2nDME} \times 100 \qquad [10]$$

where nCO_2, nCO, $nMethanol$, and $nDME$ are molar fractions of components in the outlet stream.

2.5. Stability tests for the bifunctional catalysts on DME synthesis

To determine the effects of HZSM-5 loading and mixing methods on catalyst deactivation during DME synthesis, long-term tests were performed at reaction conditions of 400 psig, 240 °C, and a flow rate of 6 sccm CO_2 and 18 sccm H_2 for 100 h. HZSM-5 loadings from 0.05 g to 0.5 g were tested with a fixed CZA loading of 0.5 g to evaluate the effects of HZSM-5 loading. To investigate the effects of mixing methods on catalyst deactivation, bifunctional catalysts composed of 0.5 g of CZA and 0.3 g of HZSM-5 were prepared by different methods and tested for DME synthesis.

Table 1
BET surface area of fresh and spent bifunctional catalysts.

Catalyst	Mixing method for bifunctional catalyst preparation	Fresh catalyst BET SA (m^2/g)	Spent catalyst BET SA (m^2/g)
CZA-HZSM-5	A	175	139
CZA-HZSM-5	B	157	136
CZA-HZSM-5	C	154	133

Table 2
Metallic properties of the spent bifunctional catalysts.

Catalyst	Mixing method for bifunctional catalyst preparation	Cu SA (N_2O) (m^2/g)	Cu dispersion (%)	Cu crystallite size (nm)
Fresh CZA-HZSM-5	A	43.0	18.3	5.7
Spent CZA-HZSM-5	A	22.8	9.7	8.9
Spent CZA-HZSM-5	B	23.9	10.3	8.5
Spent CZA-HZSM-5	C	21.2	9.0	9.6

3. Results and discussion

3.1. Characterization of catalysts

The textural and metallic properties of the fresh bifunctional catalysts are presented in Table 1 and Table 2. The prepared CZA catalyst has a BET SA of 128 m^2/g. The admixed catalyst of unpressed CZA-HZSM-5 (prepared by method A) had a BET SA of 175 m^2/g. The Cu SA was 43.0 m^2/g with Cu dispersion of 18.3 % and Cu crystallite size of 5.7 nm. These results indicate that our catalyst has a higher Cu SA than reported values [11,12]. After pressing, the BET surface area of admixed CZA-HZSM-5 catalysts prepared by method B and method C reduced to 157 m^2/g and 154 m^2/g, respectively. The decrease of surface area observed for the pressed CZA-HZSM-5 catalysts should be attributed to a mechanical stress on the structure of the catalysts, such as reducing of mesoporous [7].

The admixed calcined and reduced CZA-HZSM-5 catalysts were analyzed by XRD. As shown in Fig. 2, a strong diffraction peak at 35.5° and a weak peak at 38.7° corresponding to (002) and (1 1 1) planes of tenorite were observed for the admixed calcined CZA-HZSM-5. For the admixed reduced CZA-HZSM-5 catalyst, the diffraction peaks at 43.3°, 50.5°, and 74.1° corresponding to (1 1 1), (2 0 0), and (2 2 0) planes of copper, and diffraction peaks at 31.8°, 34.4°, 36.2°, and 56.6° corresponding to (1 0 0), (0 0 2), (1 0 1), and (1 1 0) planes of zincite were observed. These structural properties are consistent with the previous report [12]. There were no CuO peaks observed in the reduced

catalysts, indicating that CuO were reduced to metallic copper completely.

3.2. Effects of HZSM-5 loading

The effects of HZSM-5 loading on CO_2 conversion and DME synthesis were first studied, and the method A was used to prepare the bifunctional catalyst. The highest yield of DME was obtained at 240 °C with a reaction pressure of 400 psig and a gas flowrate of 24 sccm (H_2/CO_2 at 3:1). Therefore, the tests which vary the HZSM-5 loading for the bifunctional catalyst, were done at 240 °C. Fig. 3 shows that CO_2 conversion was similar with different HZSM-5 loadings (0.1 g–0.5 g) and a fixed CZA loading (0.5 g). Bonura et al. reported that DME productivity followed a volcano-shape trend for HZSM-5 loading from 0 to 100% and obtained a maximum productivity with a HZSM-5 loading of 50 wt.% [7]. However, we observed a different trend in this study. DME selectivity slightly decreased when the HZSM-5 loading reduced from 0.5 g (50 wt.% of HZSM-5 loading in bifunctional catalyst) to 0.1 g (16.7 wt.% of HZSM-5 loading), but significantly decreased when further reduced to 0.05 g (0.09 wt.% of HZSM-5 loading). DME yield kept similar when HZSM-5 loadings decreased from 0.5 g to 0.1 g, but greatly decreased when the HZSM-5 loading was 0.05 g. A similar DME yield observed with HZSM-5 loading from 0.1 g to 0.5 g could be attributed to the better surface contact between CZA and HZSM-5 prepared by method A. There were no significant changes for CO selectivity and CO yield when HZSM-5 loadings decreased from 0.5 g to 0.1 g. However, CO selectivity and yield greatly increased when the HZSM-5 loading decreased to 0.05 g. Methanol selectivity and yield showed an increasing trend with the decrease of HZSM-5 loading. As we know, the DME synthesis from CO_2 includes three main reactions: CO_2 hydrogenation to methanol, methanol dehydration, and reverse water gas shift reaction. More HZSM-5 catalyst in the bifunctional catalyst would drive the dehydration reaction to DME formation; that is why the lowest methanol yield was observed with the highest HZSM-5 loading. The insufficient HZSM-5 loading (0.05 g) limited the methanol dehydration to DME and thus enhanced the reverse water gas reaction, thereby more CO was produced.

The stability of the catalyst is an important issue in industrial processes. To better understand the effects of HZSM-5 loading on the catalyst stability, long-term stability tests with different HZSM-5 loadings were performed. The bifunctional catalysts used were prepared by method A. As shown in Fig. 4, CO_2 conversion and DME yield were almost constant at HZSM-5 loadings ranging from 0.1 g to 0.5 g (with a fixed CZA loading of 0.5 g) during a 100 h test. It indicates that there is no significant effect of HZSM-5 loading on the catalyst stability for DME synthesis. However, when we reduced the HZSM-5 loading to 0.05 g, although the CO_2 conversion was similar to those of the tests with high HZSM-5 loadings, DME selectivity and yield decreased significantly
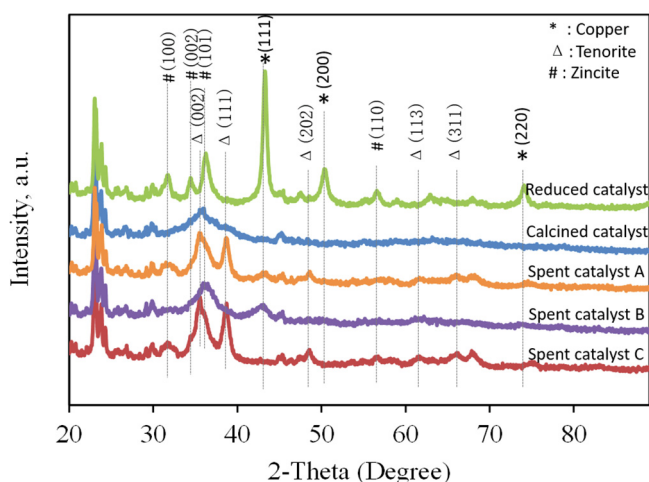

Fig. 2. XRD patterns of fresh and spent bifunctional catalysts prepared by different mixing methods. A, B, C are preparation methods for bifunctional catalysts. All bifunctional catalysts were mixed by the ratio of CZA to HZSM-5 at 0.5 g: 0.3 g.
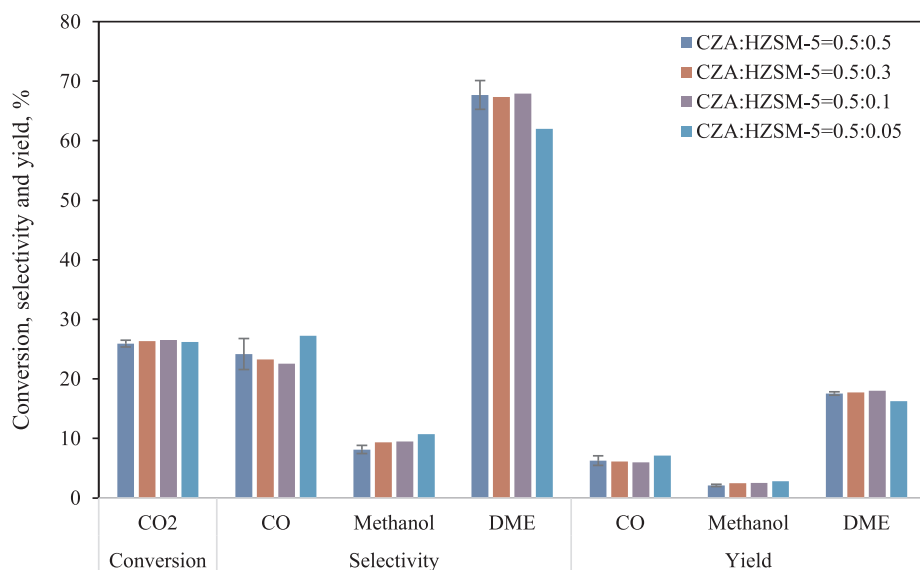
Fig. 3. Effects of the ratio of CZA and HZSM-5 on CO_2 conversion, product selectivity, and yield. The bifunctional catalysts were prepared by method A. Reaction conditions: Reaction temperature at 240 °C, reaction time: 4 h, pressure at 400 psig, 18 sccm of H_2, and 6 sccm of CO_2. Data reported are average numbers based on the 6 sampling points after reaction conditions stabilized.

with the increase of reaction time. After 50 h of reaction, the DME selectivity and yield decreased to about 30% and 7%, respectively, indicating that the insufficient dehydration catalyst loading led to a fast deactivation of catalyst.

To evaluate the effects of different HZSM-5 loadings on catalyst coking, we conducted TGA analysis for spent catalysts with a HZSM-5 loading from 0.1 g to 0.5 g (Fig. 4d). A very small amount (0.18 %) of coking was observed on the spent catalyst with 0.5 g HZSM-5. When the

HZSM-5 loading decreased to 0.3 g, the coking amount increased to 1.38 %. When we further decreased the HZSM-5 loading to 0.1 g, the coking amount was 1.48 %, similar to that of HZSM-5 loading at 0.3 g. Compared to previous reports, the coking amounts in catalysts with different HZSM-5 loadings in this study were similar to those in CO_2 hydrogenation to DME but less than those in syngas hydrogenation to DME [24,30,39]. In this study, although the lowest coking amount observed with a large loading amount of HZSM-5 (0.5 g) used for
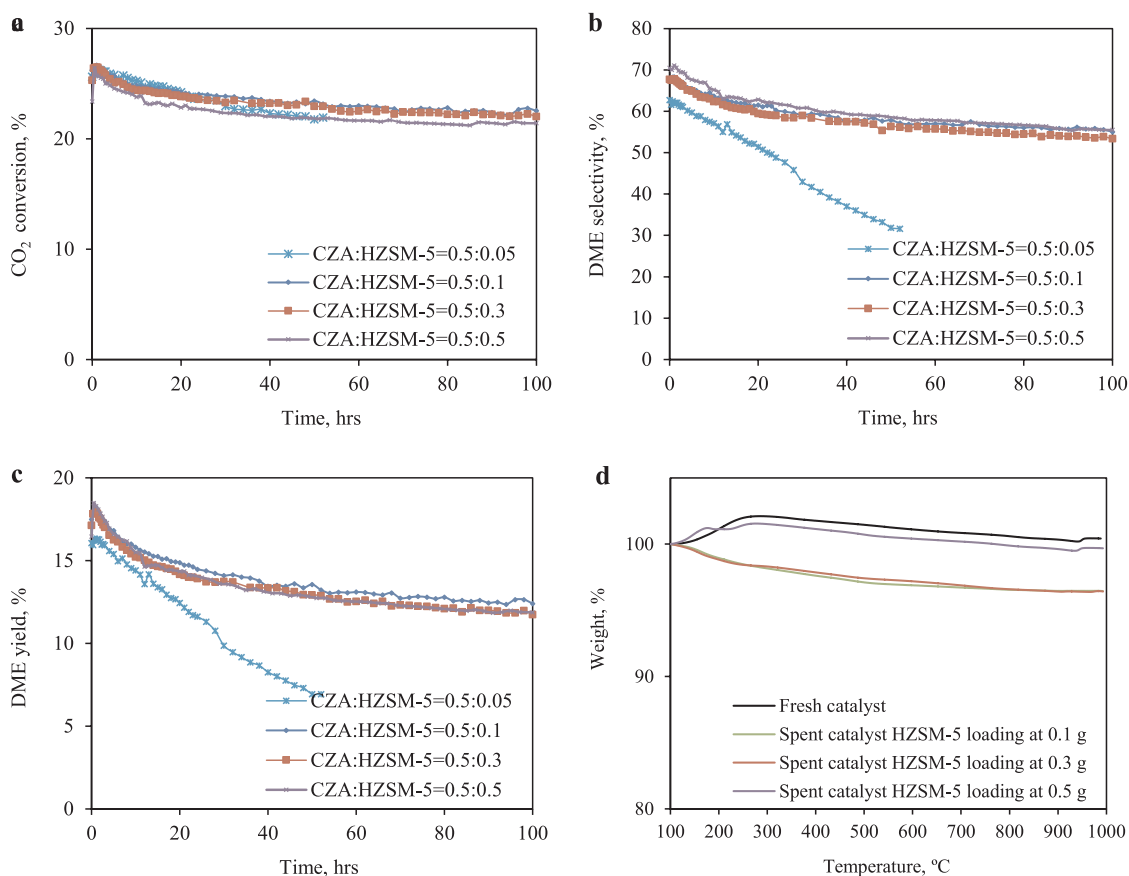

Fig. 4. (a) CO_2 conversion, (b) DME selectivity, (c) DME yield for 100 h of reaction with different catalyst ratios of CZA and HZSM-5, and (d) TGA analysis for the spent catalysts. The bifunctional catalysts were prepared by method A. Reaction conditions: Reaction temperature at 240 °C, pressure at 400 psig, 18 sccm of H_2, and 6 sccm of CO_2.
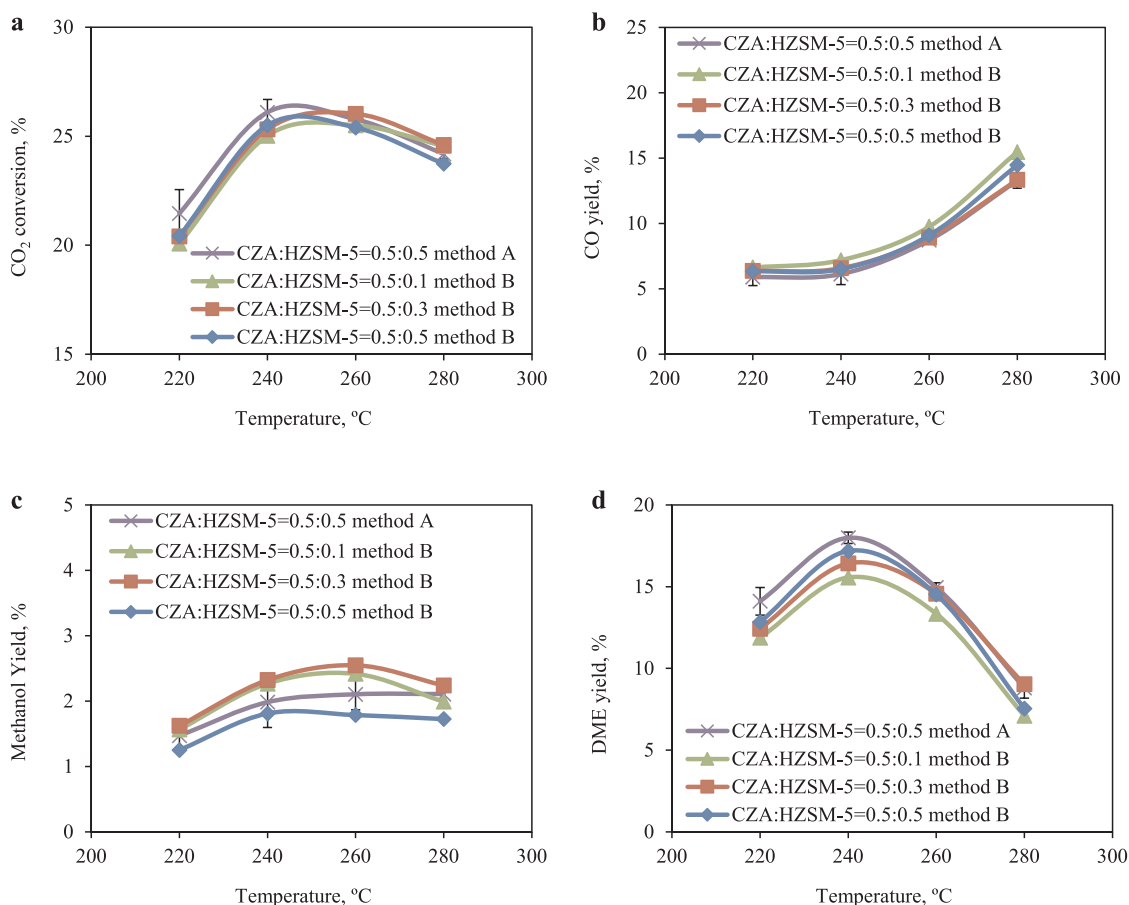
Fig. 5. Effects of mixing method B and HZSM-5 loadings on DME synthesis: (a) CO_2 conversion, (b) CO yield, (c) methanol yield, and (d) DME yield. Reaction conditions: Pressure at 400 psig, 6 sccm CO_2, and 18 sccm H_2.

preparing catalyst, the stability of catalyst was not significantly different from other catalysts with HZSM-5 loadings varying from 0.1 g to 0.3 g. These results also suggests that the minimum acceptable ratio of HZSM-5 to CZA could be 1:5 (by mass).

3.3. Effects of mixing method

The bifunctional catalysts prepared by method B with different HZSM-5 loadings (0.1 g − 0.5 g with a fixed CZA loading of 0.5 g) were tested to evaluate the effects of HZSM-5 loading on DME production. The bifunctional catalysts were tested with a fixed flow rate of 6 sccm CO_2 and 18 sccm H_2 at a reaction temperature of 220–280 °C, and pressure of 400 psig. The GHSVs were between 1525 NL/(kg h) and 2542 NL/(kg h) depending on the loading of HZSM-5. A bifunctional catalyst prepared by method A (0.5 g CZA and 0.5 g HZSM-5) was also tested at the same conditions as a reference.

As shown in Fig. 5, there were no significant changes in CO_2 conversion and CO yield at each reaction temperature between bifunctional catalysts prepared by method A and B. When the HZSM-5 loading of bifunctional catalysts prepared by method B increased from 0.1 g to 0.5 g, the CO_2 conversion and CO yield remained similar at each reaction temperature, indicating that the HZSM-5 loading has no significant effects. Methanol yields obtained using bifunctional catalysts prepared by method B were 1.3 % to 2.6% and showed a slight change compared to that of bifunctional catalysts prepared by method A. When the HZSM-5 loading in bifunctional catalysts prepared by method B was 0.5 g, methanol yields at each reaction temperature were slightly lower than those obtained from the unpressed catalysts prepared by method A. When the loading of HZSM-5 in bifunctional catalysts prepared by

method B decreased to 0.3 g and 0.1 g, methanol yields were slightly higher than those obtained from the catalysts prepared by method A. The methanol yield indicates an increasing trend with the decrease of HZSM-5 loading in bifunctional catalysts prepared by method B, which is consistent with the testing results of the catalysts prepared by method A with different HZSM-5 loadings. DME yields obtained from catalysts prepared by method B were slightly lower than those obtained from the catalysts prepared by method A. Due to the very small particle size of both catalysts, the bifunctional catalyst prepared by method A had a better surface contact between Cu active sites and acid sites. Compared to the bifunctional catalyst prepared by method A, the surface contact between Cu active sites and acid sites was reduced for bifunctional catalyst prepared by method B, which caused the slight decrease of DME yield. Further investigation of HZSM-5 loading in the bifunctional catalyst prepared by method B indicates that there was a small effect on DME yield. As we observed, the DME yield decreased with the decrease in HZSM-5 loading in bifunctional catalysts prepared by method B. At the optimum reaction temperature of 240 °C, the DME yield reduced from 17.2 % to 15.6 %, when the HZSM-5 loading decreased from 0.5 g to 0.1 g.

The activity of bifunctional catalysts prepared by method C was investigated to understand the role of better contact between Cu active sites and acid sites at interface. In order to understand the effects of HZSM-5 loading on the bifunctional catalyst preparation and DME synthesis, different HZSM-5 loadings, which were from 0.1 g − 0.5 g with a fixed CZA loading of 0.5 g, were also studied.

Fig. 6 shows the results of DME synthesis using bifunctional catalysts prepared by method C. As shown in Fig. 6, no significant differences in CO_2 conversion and CO yield at each reaction temperature
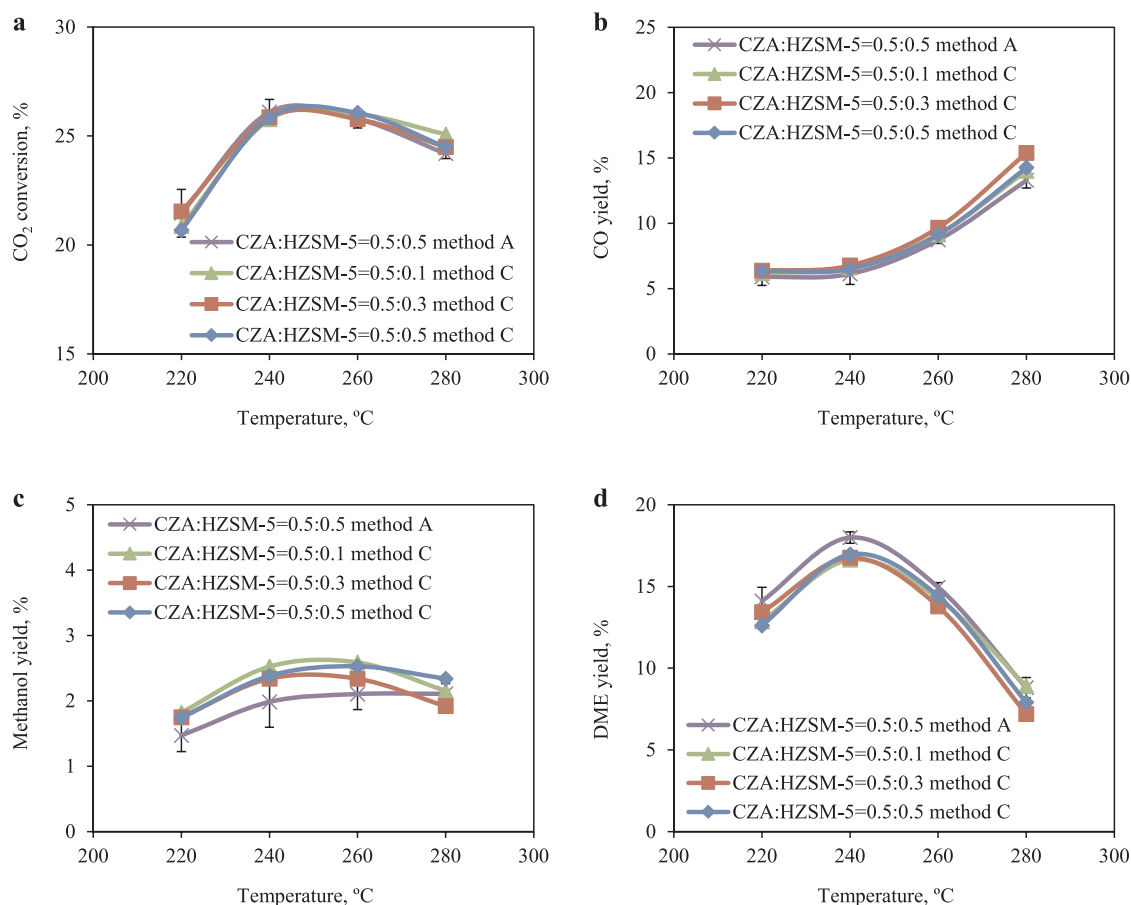
Fig. 6. Effects of mixing method C and HZSM-5 loadings on DME synthesis: (a) CO_2 conversion, (b) CO yield, (c) methanol yield, and (d) DME yield. Reaction conditions: Pressure at 400 psig, 6 sccm CO_2, and 18 sccm H_2.

were observed for the bifunctional catalysts prepared by method A and method C. However, we observed that the methanol yields slightly increased and DME yield slightly decreased compared to those of the catalysts prepared by method A. During the preparation of bifunctional catalyst by method C, the CZA and HZSM-5 powders were first mixed, as was done in the preparation of catalyst by method A (mixed by powder). The following step of pressing the bifunctional catalyst resulted in the increased yield of methanol and the decrease yield of DME. This could be due to the changes of the structure, as reflected by the slight decrease of BET surface area, and the interaction among the Cu active sites and acid sites induced by mechanical pressing. This phenomenon is similar to that observed by Bonura et al. [7].

For catalysts prepared by method C, when the HZSM-5 loading increased from 0.1 g to 0.5 g, CO_2 conversion, CO yield, methanol yield, and DME yield remained similar at each reaction temperature, indicating that the HZSM-5 loading has no significant effects. This observation is similar to those of the bifunctional catalysts prepared by method A with different HZSM-5 loadings (previous discussion in section 3.1), but different to those of bifunctional catalysts prepared by method B. The catalyst mixed by powder before being pressed could increase the contact of Cu active sites and acid sites thereby eliminating the effects of HZSM-5 loadings on DME synthesis.

3.4. Effects of mixing method on catalyst stability

To understand the effects of mixing method on the catalyst's deactivation behavior and stability, bifunctional catalysts prepared by different methods were tested at 240 °C and 400 psig for 100 h. As shown in Fig. 7, during the first 20–30 h, catalysts prepared by different mixing

methods all showed a progressive decrease of CO_2 conversion, DME selectivity and yield. The bifunctional catalyst prepared by method B had a slowest decline in CO_2 conversion compared to those prepared by methods A and C. Although method A and method C can result in better contact for CZA and HZSM-5, compared to that of the method B, CO_2 conversion of catalysts prepared by methods A and C decreased faster. The contact of CZA and HZSM-5 in bifunctional catalyst prepared by method C was more intimate due to the pressing after mixing. However, the CO_2 conversion, DME selectivity and yield at the first 20–30 h decreased even faster. After 30 h, all bifunctional catalysts prepared by different mixing methods showed a relatively slower rate of decreasing. For the catalyst prepared by method B, CO_2 conversion reduced from 26.4 % to 23.6 % and DME selectivity reduced from 64.8 % to 56.4 % after 100 h of reaction, and the DME yield reduced from 17.1 % to 13.3 %. After 100 h of reaction with a catalyst prepared by method A, the CO_2 conversion decreased from 26.2 % to 21.2 % and DME yield decreased from17.5 % to 11.7 %. The bifunctional catalyst prepared by method C showed the worst stability; CO_2 conversion reduced from 25.6 % to 20.8 %, DME selectivity reduced from 64.2 % to 48.5 %, and DME yield reduced from 16.4 % to 10.1 % after 100 h. These results indicate that the mixing method has significant effects on the catalyst stability, which is similar to previous studies for the hybrid catalysts in syngas conversion to DME [33,35]. Although method A and method C can create an intimate contact between Cu active sites and acid sites at the interface for the bifunctional catalyst, such intimate contact has negative effects on the stability of catalyst [33,35]. For the bifunctional catalysts prepared by method A and C, very small particles of CZA were used, which could block the microspores of HZSM-5 and result in the reduction of acidic sites [35]. The intimate surface contact between
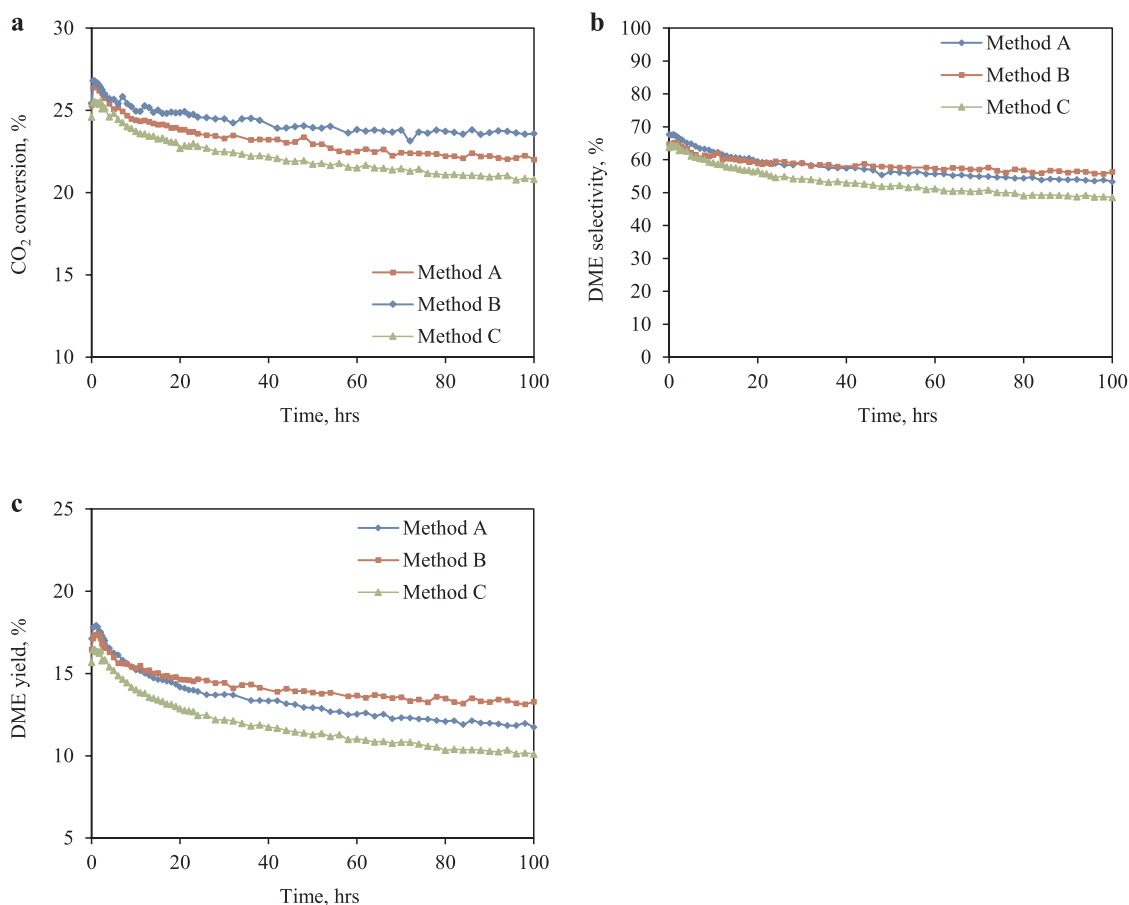
Fig. 7. Effects of different mixing methods on (a) CO_2 conversion, (b) DME selectivity, and (c) DME yield for 100 h of reaction. Reaction conditions: CZA: HZSM-5 at 0.5 g: 0.3 g, reaction temperature at 240 °C, pressure at 400 psig, 6 sccm CO_2, and 18 sccm H_2.
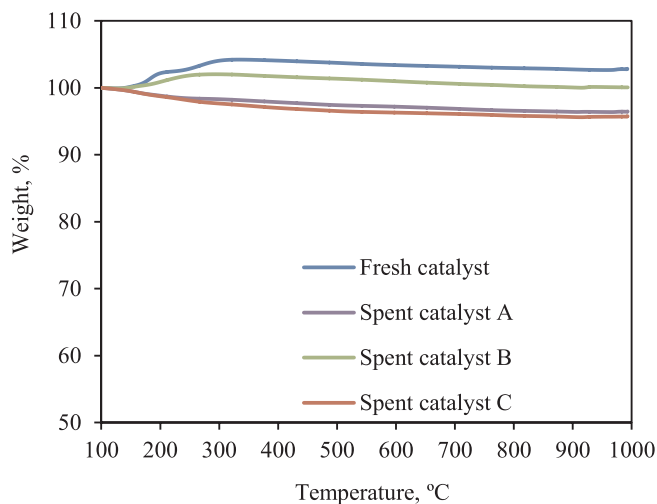

Fig. 8. TG analysis of freshly reduced catalyst and spent catalysts after 100 h of reaction at 240 °C and 400 psig. A, B, and C represent different preparation methods of bifunctional catalysts.

CZA and HZSM-5 could also induce the ion exchange of Cu^{2+} to HZSM-5 and lower the number of acidic sites [32,35,38]. Compared to syngas conversion to DME, more water is generated in the CO_2 hydrogenation step, which could contribute to the oxidation of Cu to Cu^+ or Cu^{2+} and occupy the active sites of CZA, lowering CO_2 activation and conversion [28,40].

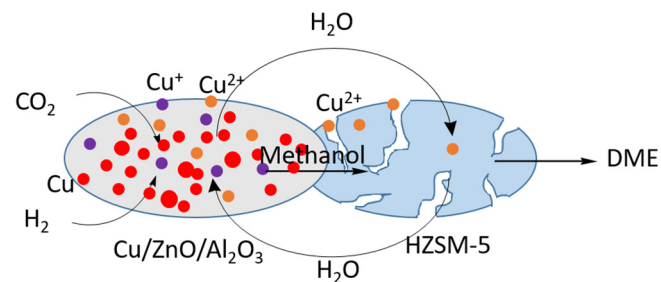To understand the deactivation mechanism of the bifunctional

Fig. 9. Possible deactivation mechanism caused by Cu sintering, Cu oxidation, and metal ions migration for bifunctional catalyst of CZA and HZSM-5 in CO_2 conversion to DME.

catalysts prepared by different mixing methods, the spent bifunctional catalysts were characterized after 100 h of reaction. As shown in Table 1, the BET surface areas of spent bifunctional catalysts significantly decreased, compared to that of fresh catalysts. This could be caused by the structural change of the catalysts or blocking of micropores of catalysts by coke or organic by-products. The spent bifunctional catalysts prepared by different mixing methods showed similar BET surface areas. The Cu surface area and Cu dispersion of spent bifunctional catalysts also greatly decreased, while the Cu crystallite size greatly increased compared to those of fresh catalysts (Table 2). It indicates that a severe Cu sintering occurred for the spent catalysts. This is consistent with a previous report [21].

According to the XRD patterns of spent bifunctional catalysts shown in Fig. 2, the active phase of Cu was significantly changed after the catalyst was used. The peaks at 35.5° and 38.7° corresponding to (0 0 2)

and (1 1 1) planes of tenorite appeared in all spent catalysts. In addition to these two peaks, another three weak peaks at 48.7°, 61.5°, and 66.3° corresponding to (2 0 2), (1 1 3), and (3 1 1) planes of tenorite were observed in the spent bifunctional catalysts prepared by method A and method C. A similar phenomena was also observed by Farbod Dadgar et al. for the spent catalyst in syngas conversion to DME [41]. These results indicate that the oxidation of Cu occurred for the catalysts during 100 h of reaction. For the spent bifunctional catalyst prepared by method B, the peak at 43.3° corresponding to (1 1 1) phase of the active site of metallic copper was observed, which means that mixing method B reduced the Cu oxidation during the long-term reaction. Compared to the other two mixing methods, the bifunctional catalyst prepared by method B reduced the surface contact between Cu active sites and HZSM-5, which could reduce the opportunity for contact of water with Cu active sizes, and thus alleviate the Cu oxidation.

The coking amounts of spent bifunctional catalysts were determined by TG. As shown in Fig. 8, the TG curves of the fresh catalyst increased slightly with the increase of temperature first, and then decreased. The increase was due to the presence of Cu, and the oxidation of Cu occurred under air during the TG analysis. The same phenomenon was observed for the spent catalyst prepared by method B. This is consistent with the XRD analysis that Cu was present in the spent catalyst. However, this phenomenon was not observed in the spent catalysts prepared by method A and method C, indicating that severe oxidation occurred during the long-term reaction. This conclusion was supported by the results of XRD analysis that there were no peaks corresponding to Cu observed in the spent catalysts prepared by method A and method C. The catalyst prepared by method B showed very little coking, with 0.86% coke after 100 h on stream. The coking amounts observed for the other two catalysts were at 1.38% (method A) and 1.31% (method C), which are slightly higher than that in the spent catalyst prepared by method B. Carcia-Trenco et al. observed carbon contents at 0.6–1.2% on hybrid catalysts prepared by different mixing methods, which were similar to our observation [33].

Fig. 9 shows a possible deactivation mechanism of bifunctional catalyst in CO_2 conversion to DME. According to the characterization of our spent catalysts, the loss of Cu active sites in CZA resulting from Cu oxidation and sintering could be one of the major causes in bifunctional catalyst deactivation besides coking. The detrimental interactions between CZA and HZSM-5 occurred in bifunctional catalysts and it could be worsened in CO_2 conversion to DME as reverse water gas shift reaction occurs and more water is generated. The presence of more water in the reaction system could also assist the Cu sintering and oxidation, and migration of Cu^+ and Cu^{2+} to HZSM-5, especially for the bifunctional catalysts with better or intimate surface contact [32,33,40]. These will eventually result in reduction of the number of Cu active sites in CZA and acidic sites in HZSM-5.

4. Conclusion

In this study, we investigated the impact of different mixing methods of CZA and HZSM-5 on DME production from CO_2 hydrogenation. The bifunctional catalysts were characterized by nitrogen adsorption and desorption, chemisorption, and XRD. The effects of HZSM-5 loading on DME synthesis and the stability of bifunctional catalyst were studied. There was no significant influence of HZSM-5 loading on DME production and catalyst stability, when the mass ratio of HZSM-5 to CZA was equal or larger than 1:5. When the mass ratio of HZSM-5 to CZA was less than 1:5, the DME selectivity and yield significantly decreased, while the CO_2 conversion was similar to those of high HZSM-5 loadings, indicating that insufficient acidic sites to convert methanol produced in CO_2 hydrogenation to DME. The activity test indicates that there was a minor effect on the DME yield when the bifunctional catalysts were prepared by method B and method C. However, the long term stability tests indicated that the mixing method had a significant influence on the catalyst stability; method B showed

the best stability and the extent of deactivation of catalysts followed the sequence of method B < method A < method C. The characterization of spent catalysts revealed that Cu oxidation and sintering occurred for the CZA catalyst. Mixing method B reduced Cu oxidation, which resulted from less surface contact between Cu active sites and HZSM-5. The results also suggested that more water generated in CO_2 conversion to DME and intimate contact between CZA and HZSM-5 catalysts could induce more severe oxidation and sintering of Cu, and metal ions migration from hydrogenation catalyst to HZSM-5, which can result in the number reduction of acidic sites.

Acknowledgements

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