Effects of Cu–ZnO Content on Reaction Rate for Direct Synthesis of DME from Syngas with Bifunctional Cu–ZnO/γ-Al$_2$O$_3$ Catalyst

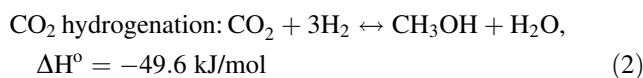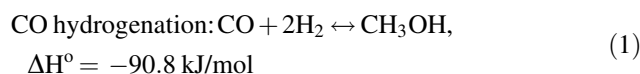**Ji Woo Jeong · Chang-Il Ahn · Dong Hyun Lee · Soong Ho Um · Jong Wook Bae**

Abstract The effects of Cu–ZnO content on the performance of bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts for dimethyl ether (DME) synthesis from syngas were investigated by varying the weight ratios of Cu–ZnO/γ-Al$_2$O$_3$ prepared by the coprecipitation of Cu–ZnO in a slurry of γ-Al$_2$O$_3$. A higher rate of DME production with CO conversion of 47.6 % and DME selectivity of 61.1 % was observed with the bifunctional catalyst at an optimal weight ratio of CuO/γ-Al$_2$O$_3$ of two, providing a higher surface area of metallic copper and an abundance of weak acid sites. The number of acidic sites on solid-acid γ-Al$_2$O$_3$ is a more crucial factor to enhance DME yield, due to the faster dehydration rate of methanol to DME than that of CO hydrogenation to methanol. Although the first step of methanol synthesis on active copper sites is a rate-limiting step with a low equilibrium value, the second step of the dehydration of methanol to DME on acid sites adjusts the overall rate by enhancing the forward reaction rate of CO hydrogenation to methanol with a simultaneous formation of surplus hydrogen by a water–gas shift reaction. Therefore, the proper design of a high surface area of metallic copper with larger acid sites on the bifunctional CuO–ZnO/γ-Al$_2$O$_3$ catalysts at an optimal ratio, produced by adjusting the weight ratio of CuO/γ-Al$_2$O$_3$, is an important factor for improved catalytic performance.
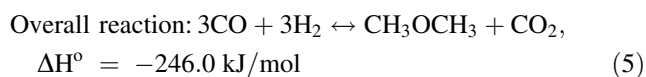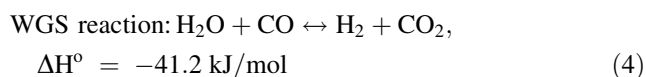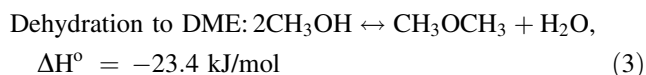
Keywords Dimethyl ether · Syngas · Copper surface area · Acidic site · CuO–ZnO/γ-Al$_2$O$_3$ · Bifunctional catalyst

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1 Introduction

The direct synthesis of dimethyl ether (DME) and higher alcohols from syngas has been largely investigated as a promising alternative method to produce renewable clean energy [1]. Renewable energy resources like DME, derived from biomass and natural gas, have a high potential to suppress the emission of CO$_2$ and air pollutants [2]. The commercialized process for DME production generally involves two steps, methanol synthesis by hydrogenation of CO$_x$, followed by consecutive DME synthesis by the dehydration of methanol. However, great interest has been focused on developing a single-step synthesis of DME using a properly designed bifunctional catalyst that contains dual functionalities for hydrogenation and dehydration [3, 4]. The direct synthesis of DME has the advantage of a high equilibrium conversion of CO by increasing the forward reaction of CO hydrogenation with surplus hydrogen formation through a water–gas shift (WGS) reaction. In addition, a single-step reaction is also suitable to use for syngas having a lower H$_2$/CO ratio, such as that frequently derived from biomass or coal gasification [4–7]. The reaction rate of DME synthesis by methanol dehydration is much faster than that of methanol synthesis by CO hydrogenation, with a higher equilibrium conversion [5]. The reactions involved and the heats of formation at 298 K for the direct synthesis of DME from syngas can be categorized as following reaction Eqs. (1) through (4), and the overall reaction can be expressed as Eq. (5):

$$\text{CO hydrogenation}: \text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}, \quad \Delta\text{H}^\text{o} = -90.8 \text{ kJ/mol} \tag{1}$$

$$\text{CO}_2 \text{ hydrogenation}: \text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}, \quad \Delta\text{H}^\text{o} = -49.6 \text{ kJ/mol} \tag{2}$$

Dehydration to DME: $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$,

$$\Delta H^o = -23.4 \text{ kJ/mol} \tag{3}$$

WGS reaction: $H_2O + CO \leftrightarrow H_2 + CO_2$,

$$\Delta H^o = -41.2 \text{ kJ/mol} \tag{4}$$

Overall reaction: $3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2$,

$$\Delta H^o = -246.0 \text{ kJ/mol} \tag{5}$$

The catalytic performances of the bifunctional catalyst are generally explained by characterizing the dispersion of copper crystallites, acidic properties of solid-acid catalyst, and adsorption behavior of reactants [6–10]. Although the reaction rates for the direct conversion of syngas to DME could be controlled kinetically at low temperatures, the rates tend to approach equilibrium values at high temperatures, and CO conversions generally decrease with the increase in temperature [4]. In addition, the hydrogenation of CO to methanol is more thermodynamically favorable than that of CO_2, and an increased CO_2 concentration in syngas generally decreases CO conversion at a fixed H_2/CO ratio according to Le Chatelier's principle, as shown in reaction equation (5) [4]. Therefore, to enhance the rate of DME production from syngas, it is crucial to design a proper bifunctional catalyst that possesses a higher copper surface area and a large number of acidic sites by simultaneously modifying the strong acidic sites on the solid-acid component [11, 12]. Many researchers have reported that CO conversion is linearly correlated with metallic copper surface areas on the admixed bifunctional catalyst, since the CO hydrogenation reaction can be a rate-limiting step in the consecutive DME synthesis reaction from syngas [13]. However, in our recent research [14], the intrinsic catalytic activity on Cu–ZnO-based bifunctional catalysts showed a good correlation between the copper surface area (S_{Cu}) and the density of acidic sites (D_{AS}), and the activity was maintained at a constant value above optimum values of ($S_{Cu} \times D_{AS}$). This also suggests that the direct synthesis of DME from syngas is a structurally insensitive reaction.

However, the effects of copper content on the catalytic activity of Cu–ZnO/γ-Al$_2$O$_3$ bifunctional catalysts have not been well explained in terms of copper surface area or number of acidic sites. Specifically, the number of acidic sites largely influences the overall reaction rate of CO hydrogenation by promoting a faster dehydration rate of methanol to DME, and the abundant presence of methanol on the bifunctional catalyst surfaces could also enhance the overall reaction rate due to the lowest activation barrier for the pathway involving the adsorption of two methanol molecules, as reported by Blaszkowski and van Santen [15]. Therefore, the higher overall reaction rate of DME synthesis from syngas on bifunctional catalysts can be mainly attributed to the presence of a larger number of acidic sites rather than a higher metallic copper surface area, since the rate of methanol dehydration to DME is faster than that of CO hydrogenation to methanol [5, 13, 16].

In the present study, we investigated the effects of Cu–ZnO content on the catalytic performance of Cu–ZnO/γ-Al$_2$O$_3$ bifunctional catalysts for the single-step synthesis of DME from syngas, varying the copper surface areas and the number of acidic sites using coprecipitation of Cu–ZnO in a slurry of the solid acid component of γ-Al$_2$O$_3$. The catalytic activities were significantly affected by simultaneously varying the copper surface area and acid sites, as mentioned in our previous work on the Cu–ZnO–Al$_2$O$_3$/Zr-modified ferrierite catalytic system [14], and the role of acidic sites was more dominant in the bifunctional catalysts for a higher rate of DME synthesis. The optimum ratio of active metals and solid acid components also depends on the acid strength of the solid-acid catalysts, and a much lower fraction of zeolite to active Cu–ZnO metals has been reported as an optimal composition for a higher DME yield on bifunctional catalysts compared with the solid-acid catalyst of Al$_2$O$_3$ [17]. The correlations of copper surface area and number of acid sites to catalyst performance using a simple Cu–ZnO/γ-Al$_2$O$_3$ bifunctional catalytic system for 20 h were characterized by X-ray diffraction (XRD) analysis, N$_2$O titration, and the temperature-programmed desorption of NH$_3$ (NH$_3$-TPD) on bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts.

2 Catalyst Preparation, Characterization and Activity Tests

The solid-acid catalyst of γ-Al$_2$O$_3$ for the methanol dehydration reaction to DME has a surface area of around 230 m^2/g with an average pore diameter of 19 nm and was supplied by Saint-Gobain. The bifunctional catalysts were prepared by the co-precipitation method in a slurry of γ-Al$_2$O$_3$ at 70 °C using metal precursors of copper acetate and zinc acetate with Na$_2$CO$_3$ precipitant at a fixed molar ratio of CuO/ZnO = 3/1 and a final solution pH around 7. The copper surface area and number of acid sites were controlled by varying the CuO/γ-Al$_2$O$_3$ weight ratio from 1.13 to 6.75. The precipitate was aged for 3 h at 70 °C followed by calcination at 300 °C for 5 h. The bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts are denoted as CZA(X), where C, Z, and A represent CuO, ZnO, and solid-acid γ-Al$_2$O$_3$, respectively, and X denotes the weight ratio of CuO/γ-Al$_2$O$_3$ such as CZA(1), CZA(2), CZA(4), and CZA(7) for 1.13, 1.75, 4.25, and 6.75, respectively. The catalytic properties of the bifunctional catalysts are easily adjusted by changing a weight ratio of CuO-ZnO/γ-Al$_2$O$_3$, and the

coprecipitation of active metals in a slurry of the solid-acid component of γ-Al_2O_3 is the more effective method compared with the physical mixing of two active catalysts, due to the easy control of strong acidic sites through a deposition–precipitation method [7, 10].

The catalytic performance was tested in a fixed bed tubular reactor with an outer diameter of 12.7 mm using a catalyst loading of 0.2 g. Prior to reaction, the bifunctional catalysts were reduced in a flow of 5 vol% H_2 balanced with N_2 at 300 °C for 5 h. The syngas was composed of an H_2/CO molar ratio of 2.0 with an internal standard gas of 5.6 mol% N_2 based on total syngas. The reaction was carried out for around 20 h on stream with the following reaction conditions: T = 270 °C, P = 3.5 MPa, and space velocity = 2,000 ml/g_{cat} /h. The CO conversion and product distribution were obtained from the steady-state average values over 5 h after 15 h of reaction. The products were analyzed using an online gas chromatograph (Younglin GC, YL6100) using a Porapack-Q column connected to a thermal conductivity detector (TCD) to analyze N_2, H_2, CO, and CO_2 and a GS-Q column connected to a flame-ionized detector to analyze methanol, DME, and hydrocarbon byproducts.

The bifunctional CZA catalysts were characterized by temperature-programmed reduction (TPR) experiments. Each catalyst was pretreated with a He flow up to 200 °C for 1 h to remove the adsorbed water and other contaminants, followed by cooling to 50 °C. A 5 vol% H_2/He mixture was introduced in the BELCAT instrument at a flow rate of 30 ml/min with a heating rate of 10 °C/min up to 500 °C. The effluent gas was passed through a molecular sieve to remove water formed during the TPR experiment, and it was analyzed by TCD. The temperature-programmed desorption of ammonia (NH_3-TPD) was also carried out on fresh bifunctional CZA catalysts to determine the surface acidity. Around 0.1 g of catalyst was initially flushed with a He flow at 250 °C for 2 h, then cooled to 100 °C and saturated with NH_3. After the NH_3 exposure, the catalyst was purged under a He flow until it reached an equilibrium point and was then subjected to a TPD experiment in the temperature range of 100–600 °C with a heating rate of 10 °C/min using the same BELCAT instrument.

The Brunauer–Emmett–Teller (BET) surface area of the bifunctional CZA catalysts was measured by the nitrogen adsorption method at −196 °C using a constant-volume adsorption apparatus (Micromeritics, ASAP-2400). The surface area of the metallic copper was measured by the N_2O surface titration method. Prior to N_2O titration, the catalyst was reduced at 300 °C for 5 h with 5 vol% H_2/N_2 mixed gases at a flow rate of 30 ml/min, and consumption of N_2O with a concomitant release of N_2 onto the metallic copper sites ($N_2O + 2Cu = Cu_2O + N_2$) was analyzed by a BELCAT instrument equipped with a TCD. The surface

area of metallic copper on the bifunctional CZA catalysts after reaction for 20 h was calculated by assuming 1.46×10^{19} Cu atoms/m^2 with a molar ratio of 0.5 for N_2O/Cu_s (where Cu_s is a Cu atom on the surface) [18].

The crystallite size of the copper species before and after reaction was also characterized by powder XRD analysis using a Rigaku diffractometer with CuKα radiation in order to identify the phases of metallic Cu, CuO, ZnO, and γ-Al_2O_3. The average crystallite size of the copper species was calculated from the values of the full width at half maximum (FWHM) of the XRD diffraction peaks at $2\theta = 35.6°$ for CuO for fresh catalysts and $2\theta = 43.3°$ for the metallic copper (Cu^0) on the used catalysts.

3 Results and Discussion

3.1 Catalytic Performance and Characteristics of Bifunctional CZA Catalysts

The results of the catalytic performances at steady state are summarized in Table 1. CO conversion and DME selectivity were found to be highest for CZA(2), with values of 47.6 and 61.1 mol%, respectively. The CO conversion was somewhat lower than the calculated equilibrium CO conversion of around 75 % at 270 °C and 3.5 MPa, which was calculated using the HSC Chemistry 7.0 simulator. The lowest CO conversion and DME selectivity were observed for CZA(7), which contained a higher CuO/γ-Al_2O_3 ratio, with values of 19.0 and 24.7 mol%, respectively. The overall reaction rates (reacted CO mol/g_{cat}/s) were found to be in the range of 0.57–1.42. The reaction rate was increased with an increase of CuO–ZnO/γ-Al_2O_3 up to two, and it was decreased to 0.57 for CZA(7). Therefore, the overall reaction rate and yield of DME were maximized for CZA(2), and the methanol selectivity was inversely proportional to CO conversion on the bifunctional CZA catalysts. CO_2 selectivity was also proportional to the extent of CO conversion due to enhanced WGS reaction activity. The simultaneously formed surplus hydrogen on the CZA catalysts can enhance the reaction rate and CO_2 selectivity together, and the byproduct formation was related to the CO conversion by the possible reforming reaction of the products [6, 10]. Although the performance of the CZA catalysts seems to have no significant relationship with copper content, the CO conversion and DME yield on the CZA catalysts may be strongly related to two factors, the surface area of metallic copper for CO hydrogenation and the number of acidic sites for the dehydration of methanol in a consecutive reaction of direct DME synthesis from syngas through the intermediate formation of methanol.

Table 1 Catalytic performances over the bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts

Notation[a]	CO conv. (mol%)	Reaction rate[b]/10^{-2}	Selectivities (mol%)				Yield of DME
			Methanol	DME	CO$_2$	BP[c]	
CZA(1)	42.7	1.27	28.0	56.2	12.2	3.6	24.0
CZA(2)	47.6	1.42	17.3	61.1	17.4	4.1	29.1
CZA(4)	28.4	0.85	27.3	53.3	14.8	4.6	15.1
CZA(7)	19.0	0.57	67.6	24.7	5.3	2.4	4.7

[a] The bifunctional catalysts are denoted as CZA(X), where C, Z, and A represents CuO, ZnO, and solid-acid γ-Al$_2$O$_3$, and X denotes a weight ratio of CuO/γ-Al$_2$O$_3$ at a fixed CuO/ZnO molar ratio of three

[b] The reaction rates of DME synthesis from syngas are defined as reacted CO mol/g$_{cat}$/s, which are the average values at steady-state

[c] Byproducts (BP) mainly include CH$_4$ and a trivial amount of C$_2$ hydrocarbons

Table 2 The characteristics of the bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts

Notation	Weight ratio of (CuO/γ-Al$_2$O$_3$)	Surface area (m^2/g)	XRD (crystallite size, nm)		Acid sites (D(AS)) (mmol NH$_3$/g)[a]			Cu surface area (S(Cu)) (m^2/g$_{Cu}$)[b]
			CuO (fresh)	Metallic Cu (used)	Peak T$_1$ (<300 °C)	Peak T$_2$ (300–500 °C)	Total (T$_1$ + T$_2$)	
CZA(1)	1.13	95.3	11.8	32.3	0.514	0.428	0.942	3.47
CZA(2)	1.75	91.8	10.6	24.2	0.468	1.038	1.506	6.25
CZA(4)	4.52	88.1	11.7	27.8	0.355	1.011	1.466	5.48
CZA(7)	6.75	85.7	14.5	36.3	0.321	0.437	0.758	5.90

[a] The acidic site density (D(AS)) was calculated from the desorption peak areas for NH$_3$-TPD, and they are assigned at the regions of 100–300 °C (T$_1$) and 300–500 °C (T$_2$), respectively

[b] The copper surface area (defined as S$_{Cu}$ = exposed metallic copper area (m^2/g) per gram of catalyst) of S(Cu)) after reaction was measured by N$_2$O titration method

As shown in Table 2, the surface areas of the bifunctional CZA catalysts were in the range of 85–96 m^2/g, and they decreased slightly with the increase in the CuO/γ-Al$_2$O$_3$ weight ratio due to the possible blockage of mesopores of the solid-acid γ-Al$_2$O$_3$ by the deposition of CuO–ZnO crystallites on surfaces. As shown in Fig. 1, TPR profiles of the CZA catalysts exhibited only one broad reduction peak at a maximum reduction peak of around 165 °C, without displaying any shoulder peaks below 250 °C. However, the peak did get broader in the shape of a skewed Gaussian distribution with the increase in the CuO/γ-Al$_2$O$_3$ weight ratio, and this could suggest the formation of a larger size of heterogeneously-distributed CuO–ZnO crystallites on the surface of γ-Al$_2$O$_3$ [6], especially in CZA(7), which had a high temperature reduction peak due to its large copper content. The lowest reduction temperature was observed for CZA(2), and this also suggests a homogeneous dispersion of CuO–ZnO crystallites due to its Gaussian distribution. TPR profiles of the CZA catalysts also suggest that the CuO species were well distributed on the γ-Al$_2$O$_3$ surface by the formation of a CuO–ZnO matrix [10, 11], and this homogeneous distribution with a small crystallite size on CZA(2) was
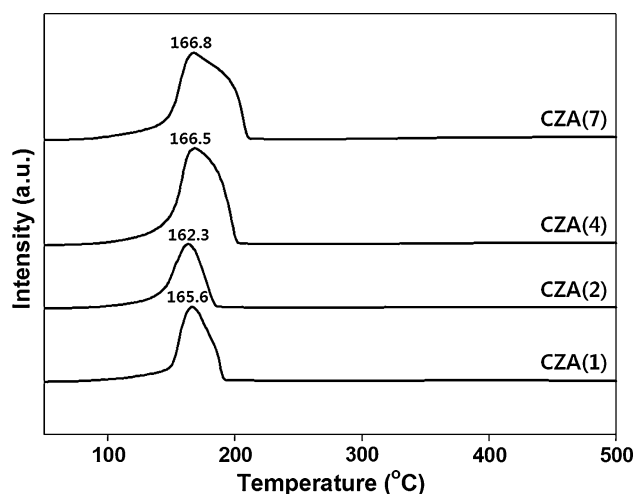
Fig. 1 TPR profiles on the bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts

responsible for the suppressed aggregation of copper crystallites during the 20 h reaction duration. The crystallite size of CuO on CZA catalysts was characterized by XRD analysis on fresh CZA catalysts, and the results are summarized in Table 2 and Fig. 2a. The crystalline phases
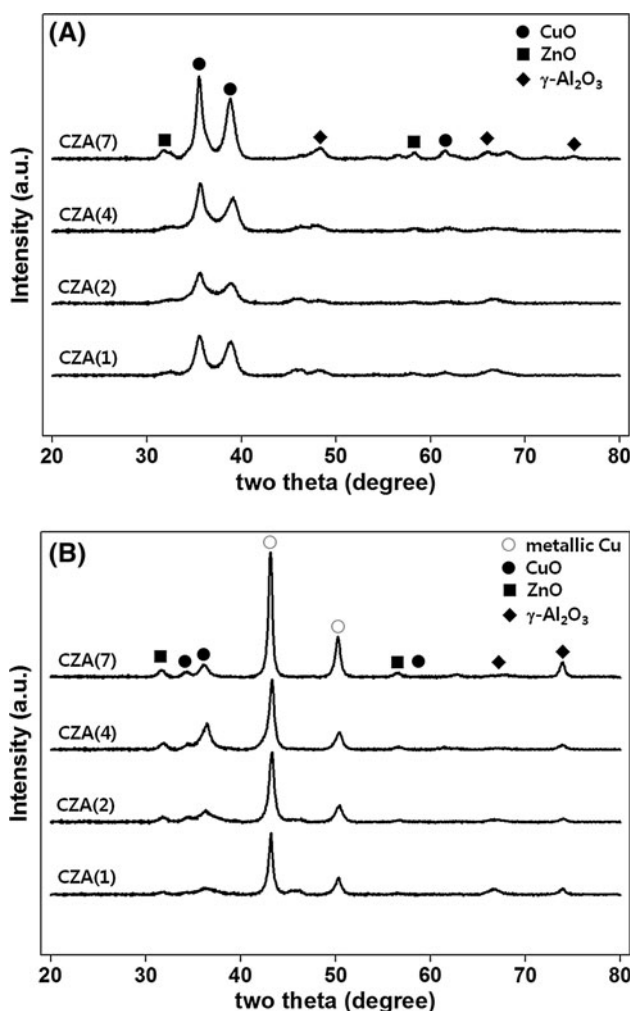
Fig. 2 XRD patterns of the fresh and used bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts **a** fresh CZA catalysts, **b** used CZA catalysts

of CuO, ZnO, and γ-Al$_2$O$_3$ were observed on all fresh catalysts, and the calculated crystallite size was in the range of 10.6–14.5 nm. The smallest crystallite size of CuO was observed on CZA(2), with a size around 10.6 nm, which corresponded to the lower reduction temperature with a Gaussian distribution in the TPR experiment.

The acidic properties of bifunctional CZA catalysts were characterized by NH$_3$-TPD, and the summarized results are also included in Table 2. The desorption temperatures of NH$_3$ were correlated with the extent of surface acidity for the activity for methanol dehydration to DME. The desorption patterns of NH$_3$ (not included) showed two distinguishable peaks, the T$_1$ peak below 300 °C and the T$_2$ peak in the range of 300–500 °C. According to our previous investigations [7–10], the T$_1$ peak corresponds to the acidity attributed to the weakly acid sites from the γ-Al$_2$O$_3$ support matrix, and the T$_2$ peak corresponds to the desorption of strongly adsorbed NH$_3$ on CuO–ZnO or γ-Al$_2$O$_3$ acidic sites. In addition, the observed sharp peak

above 800 °C is assigned to the desorption of water molecules by possible structural collapse of the main frameworks of γ-Al$_2$O$_3$ and CuO–ZnO. Consequently, only the T$_1$ and T$_2$ peaks were assigned to the active sites for methanol dehydration to DME. The concentration of weak acid sites for the T$_1$ peak decreased from 0.514 to 0.321 mmol NH$_3$/g with an increase in the CuO/γ-Al$_2$O$_3$ weight ratio by the deposition on γ-Al$_2$O$_3$ surface, and this was also confirmed by the observed decrease in BET surface area. The T$_2$ peak assigned to the strong acidic sites was maximized for CZA(2), with 1.038 mmol NH$_3$/g, and the summation of the acidic sites (T$_1$ + T$_2$) [denoted as D(AS)] for the active sites of methanol dehydration to DME was also maximized on CZA(2), with 1.506 mmol NH$_3$/g, showing the shape of a volcano curve. This is mainly attributed to the degree of dispersion of the copper crystallites and the pore blockage of the Al$_2$O$_3$ surface, and the smaller crystallite size of copper oxide and a lower degree of pore blockage were characteristic of CZA(2).

3.2 Effects of the Copper Surface Area and Acidic Sites

Although the characteristics of bifunctional CZA catalysts before reaction are important to describe the catalytic activity at the beginning of reaction, the physicochemical properties of the used bifunctional CZA catalysts are more convincing to explain the different catalytic performances. Therefore, the used bifunctional CZA catalysts were further characterized by XRD and N$_2$O titration methods to measure their copper surface areas and crystallite sizes. On industrial Cu–ZnO–Al$_2$O$_3$ catalyst for CO hydrogenation to methanol, metallic coppers are known to be active sites, and ZnO and Al$_2$O$_3$ act as structural promoters to enhance the dispersion of copper crystallites and to suppress the aggregation of copper crystallites, which is affected by the composition of Cu–ZnO–Al$_2$O$_3$ and the synthesis conditions [19, 20]. As shown in Fig. 2b and Table 2, the copper crystallites were significantly aggregated after 20 h of reaction, as indicated by the increased peak intensity of the XRD patterns, and the calculated crystallite size of metallic copper was in the range of 24.2–36.3 nm. The smallest crystallite size of 24.2 nm was observed on CZA(2), with a low sintering character, and the larger crystallite formation was observed on CZA(7), which had a higher copper content. This is also supported by the observed high surface area of metallic copper [denoted as S(Cu)] with a value of 6.25 m^2/g$_{Cu}$ on CZA(2) after reaction, as measured by the N$_2$O titration method and summarized in Table 2. The surface area of metallic copper was in the range of 3.47–6.25 m^2/g$_{Cu}$, and the area was in the shape of a volcano curve, showing a slight decrease above the CuO/γ-Al$_2$O$_3$ weight ratio of 1.75. Although the surface area of

copper as well as the number of acidic sites were found to be in the shape of a volcano curve, the decline in acidic site density was more significant with the increase in CuO/γ-Al$_2$O$_3$ weight ratio. This could be attributed mainly to the abundant presence of CuO–ZnO crystallites on the outer surface of γ-Al$_2$O$_3$, where they blocked mesopores. Therefore, a larger metallic surface area of copper and larger number of acidic sites on CZA catalysts could be simultaneously responsible for a higher catalytic activity [13, 14].

On CZA(2), which showed a higher CO conversion and DME selectivity, the number of acidic sites assigned to peaks of I and II (below 500 °C) and the surface area of metallic copper after reaction were the largest among the catalysts, with values of 1.506 mmol NH$_3$/g and 6.25 m^2/g, respectively. The enhanced CO conversion on the bifunctional CZA catalysts was due to the fast consumption rate of methanol during its dehydration to DME, with the surplus hydrogen formation through the WGS reaction overcoming an equilibrium conversion of CO. The observed lower CO conversion with CZA(7) could be attributed to a lower number of acidic sites for a lower rate of methanol dehydration. In addition, the hydrocarbon formation was slightly greater for CZA(2) and CZA(4) due to the abundant presence of acidic sites, which are possible active sites for methanol or DME reforming reactions [6, 10, 14, 21, 22]. Therefore, the performance of the CZA catalysts depends simultaneously on the surface area of metallic copper and the number of acidic sites, but their contributions could be somewhat different.

As shown in Fig. 3, the reaction rate of the CO conversion to DME was strongly related to the number of acidic sites as well as the metallic copper surface area. The maximum reaction rate was observed with CZA(2), which possessed a higher copper surface area and acidic site
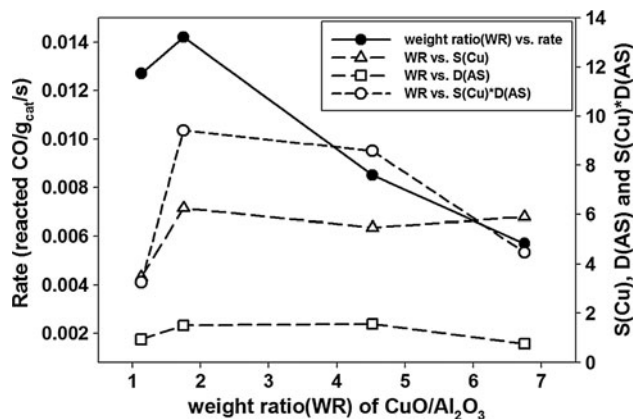

Fig. 3 Correlation of reaction rates versus the number of acid sites (D(AS)), surface area of metallic copper after reaction (S(Cu)), and their product values (D(AS) × (S(Cu)) on bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts

density. The increased CO conversion on CZA(2) is mainly attributed to a larger number of acidic sites rather than a higher surface area of copper, since the decrease in surface area with the increase in the CuO/γ-Al$_2$O$_3$ weight ratio was not significant, but the increase in the number of acid sites was significant. Therefore, the overall rate of CO conversion in this consecutive DME synthesis reaction could be predominantly controlled by the rate of methanol dehydration to DME, as compared to the CO hydrogenation rate to methanol. As suggested by Blaszkowski and van Santen RA [15], the lowest activation barrier for an adsorption pathway of two methanol molecules is responsible for the facile formation of DME by the dehydration of methanol compared to methoxy formation from one adsorbed methanol molecule. Therefore, the observed increase in DME selectivity with a higher CO conversion for CZA(2) could be attributed to the fast dehydration rate of methanol to DME due to the abundant formation of methanol on the active copper metal surfaces. Although the copper surface area on the bifunctional CZA catalysts could be significantly enhanced by the small crystallite size of the copper species with a high surface area on CZA(2), the total number of acidic sites significantly contributed to the overall reaction rate for direct DME synthesis from syngas. This is also supported by the observation of a lower rate with CZA(7), which possessed a higher metallic surface area of copper (5.90 m^2/g$_{Cu}$) and a smaller number of acidic sites (0.758 mmol NH$_3$/g). These characteristics of CZA(7) were possibly induced by acidic site blockage by the deposition of small Cu–ZnO crystallites on γ-Al$_2$O$_3$ surface, which resulted in a lower overall CO conversion.

The simultaneous consideration of the surface area of metallic copper and the number of acidic sites showed a good correlation for the simply prepared Cu–ZnO/γ-Al$_2$O$_3$ catalysts, which is in agreement with the results of our previous work [14], and the correlations of the values of S(Cu) × D(AS) with the reaction rate are well explained for the bifunctional CZA catalysts, rather than the correlations with the values of S(Cu) or D(AS) alone, as shown in Fig. 3. In addition, the number of acidic sites exposed on solid-acid γ-Al$_2$O$_3$ is a more crucial factor to obtain a higher DME yield on bifunctional CZA catalysts than the surface area of metallic copper due to the fast dehydration rate of methanol to DME.

4 Conclusions

CO conversion and DME selectivity with bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts for the direct synthesis of DME from syngas were strongly related to the surface area of metallic copper and the number of acidic sites; however, the overall conversion of CO in this consecutive reaction is

predominantly controlled by the rate of methanol dehydration to DME as compared to hydrogenation rate of CO to methanol. From the present observation, the number of acidic sites is a more crucial factor to enhance DME yield with bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts. The significant increase in the reaction rate for the direct CO conversion to DME is mainly attributed to the presence of a large number of acidic sites created by optimizing the CuO/γ-Al$_2$O$_3$ weight ratio at around two and by enhancing the consumption rate of the methanol dehydration to DME. The design of a high surface area of metallic copper with abundant acidic sites during the coprecipitation step are important factors for obtaining a higher catalytic performance, and the contribution of acidic sites is more dominant for the overall reaction rate with bifunctional Cu–ZnO/γ-Al$_2$O$_3$ catalysts.

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