Synthesis of Dimethyl Ether via CO₂ Hydrogenation: Effect of the Drying Technique of Alumina on Properties and Performance of Alumina-Supported Copper Catalysts

Chalida Niamnuy,* Pawanrat Prapaitrakul, Noppadol Panchan, Anusorn Seubsai, Thongthai Witoon, Sakamon Devahastin, and Metta Chareonpanich

ABSTRACT: Thermal treatment during catalyst preparation is one of the important factors affecting the characteristics and performance of a catalyst. To improve the catalytic performance of an alumina-supported copper catalyst prepared by an impregnation method for dimethyl ether (DME) synthesis from CO₂, the effects of the use of hot air and infrared drying as well as calcination at 600 and 900 °C to prepare alumina supports were investigated. Infrared drying could shorten the required drying time by 75% when compared with hot air drying. Infrared drying could also help maintain the pore size and pore volume of the supports, leading to their larger surface areas. Different drying techniques were additionally noted to result in different sizes and shapes of the pores as well as to different copper distributions and intensities of acid sites of the catalyst. An increase in the calcination temperature resulted in a decrease in the surface area of the supports because of particle aggregation. The drying technique exhibited a more significant effect than calcination temperature on the space-time yield of DME. A catalyst utilizing the support prepared by infrared drying and then calcined at 600 °C exhibited the highest yield of DME (40.9 gDME kgcat⁻¹ h⁻¹) at a reaction temperature of 300 °C. Stability of the optimal catalyst, when monitored over a 24 h period, was noted to be excellent.

1. INTRODUCTION

During the past decade, climate change and, in particular, global warming have been of increasing concern.¹–³ Such changes are primarily because of the emission of carbon dioxide (CO₂) into the atmosphere; the emission is partly because of combustion of fossil fuels to generate electricity, which is in increasing demand globally.⁴ One feasible and sustainable strategy to reduce CO₂ emission is to convert the gas into valuable products that can be used as fuels and chemical feedstocks, including methanol and dimethyl ether (DME).⁵

DME is considered an environmentally friendly fuel compound as it does not produce nitrogen oxides (NOₓ) and coke upon combustion. DME also possesses a significantly higher cetane number (ca. 55–60) than diesel.⁶ In addition to being a greener fuel compound, DME also exhibits many other chemical application potentials, including being an intermediate for the production of methyl acetate and dimethyl sulfate as well as being a replacement compound for chlorofluorocarbons, among others. Synthesis of DME from CO₂ has therefore received much research attention as doing so would not only reduce CO₂ emission into the atmosphere but also allow conversion of CO₂ into useful chemicals.

CO₂ conversion into DME using a heterogeneous catalyst can be conducted via two sequential processes. Hydrogenation reaction is the first process to synthesize methanol from CO₂ (eq 1); reverse water gas shift reaction can nevertheless simultaneously occur (eq 2). The second process is the dehydration reaction to synthesize DME from methanol (eq 3).

$$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H^\circ = -49.4 \text{ kJ mol}^{-1} \quad (1)$$

$$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H^\circ = +41.2 \text{ kJ mol}^{-1} \quad (2)$$

$$2\text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad \Delta H^\circ = -23.4 \text{ kJ mol}^{-1} \quad (3)$$
Alumina is widely used as a catalyst support for DME synthesis reaction as alumina possesses higher surface area, thermal and mechanical stabilities, and surface acidity. Moreover, pore sizes of an alumina support can be manipulated over a wider range, from meso to macro scales. The most popular catalyst for the synthesis of DME from CO₂ is alumina-supported copper (Cu/Al₂O₃) catalysts, which can provide DME yields in the range of 20–40 gDME kgcat⁻¹ h⁻¹.²³ Such a catalyst is considered a bi-functional catalyst as it allows both methanol synthesis and formation of DME in a single reactor. During the course of the reaction, CO₂ is initially converted into methanol via hydrogenation over the Cu surface. Methanol is then immediately transformed to DME via dehydration over acid sites of the alumina surface.⁹

During catalyst preparation, drying and calcination are known to be the important steps that strongly affect the textural properties of a catalyst (in such terms as surface area, pore size, and pore volume); distribution of the active metal on a support;¹⁰,¹¹ and interaction between active sites and a support are also known to be affected by these two preparation steps.¹² While hot air drying has traditionally been used for catalyst preparation, alternative drying techniques such as freeze drying and microwave drying have also been studied.¹⁰,¹³–¹⁶ Different drying techniques and conditions have noted to differently affect the pore size, Brunauer–Emmett–Teller (BET) surface area, dispersion of metal on a support, and hence the performance of a catalyst.¹⁷,¹⁸ Albretsen et al.,¹⁹ for example, reported that an iron-based catalyst dried at 130 °C had larger pore volume, surface area, extent of reduction, and Fischer–Tropsch synthesis rate but lower methane selectivity compared to identical catalysts dried at higher or lower temperatures. Villegas et al.²⁰ found that metal dispersions, especially in the case of Ni, were strongly influenced by the applied drying method; Ni dispersion was more homogenous upon microwave drying or ambient-temperature drying than in the case of oven drying. The drying method then naturally affected the performance of the catalysts during autothermal reforming of isooctane.

Fewer studies are available regarding the thermal treatment of a catalyst support. Among the available studies, Keyvanloo et al.²¹ investigated the effect of calcination temperature on the properties of iron catalyst supported on silica-stabilized alumina (Fe/Al₂O₃) for Fischer–Tropsch synthesis reaction. The supports calcined at 1100–1200 °C were noted to be more highly reducible, more effectively carbided, and highly reactive for Fischer–Tropsch synthesis than those traditionally calcined at 500–800 °C. Lind et al.²² prepared porous alumina via spray drying of nonporous alumina particles; the spray-dried porous alumina was used as a support for cobalt- and rhenium-based Fischer–Tropsch catalysts. Agglomeration of nonporous alumina particles during spray drying was noted to result in an alumina support with higher porosity.

Despite the aforementioned studies, the effect of drying technique of alumina support on the properties of an alumina-supported metal catalyst has never been investigated. Because infrared drying is known to exhibit higher heat transfer efficiency and hence higher drying rate,²³ it was postulated that infrared drying should be able to positively modify the pore structure of the support, leading to improved catalyst performance. Characteristics and catalytic activity of copper catalyst prepared from the infrared-dried alumina support for the synthesis of DME from CO₂ were therefore investigated; the results were compared with those of the catalyst prepared from the hot air-dried support. The effect of calcination temperature (600 and 900 °C), which is the required step after drying, of the alumina supports was also investigated.

2. RESULTS AND DISCUSSION

2.1. Drying Kinetics of Alumina Supports. Two drying techniques viz. hot air drying and infrared drying were used to prepare alumina (Al₂O₃) supports; drying was conducted at 40 °C in all cases. The prepared supports were denoted as Al_HAD and Al_IRD.

Drying curves of the supports undergoing the two drying processes are shown in Figure 1. Initial moisture content of the supports was 725% (dry basis); the final moisture content was 22.5% (dry basis). The required drying time in the case of hot air drying was 235 h, while that in the case of infrared drying was only 59 h; saving of as much as 75% in the drying time was noted when infrared drying was used. This is ascribed to the fact that infrared radiation could directly penetrate the matrix of alumina; water molecules in the matrix directly received the energy and vibrated, resulting in rapid evaporation of water. On the other hand, the water molecules in the matrix undergoing hot air drying received the energy by conduction, which is a slower and less-efficient process than radiation. This resulted in turn in much slower water removal. More extensive moisture gradients also existed in the case of hot air drying as moisture gradients also existed in the case of hot air drying as the outer layers of the matrix dried much earlier than the inner layers. This is because conduction took place from the outer to the inner layers of the matrix. As a result, the pores of Al_HAD were expected to suffer more collapse, leading to smaller average pore size and pore volume.²⁴,²⁵ Such an expectation is well verified by the scanning electron microscopic images and BET analysis results, which will be discussed in the next section.

2.2. Effects of Drying Techniques and Calcination Temperature on Physicochemical Properties of the Alumina-Supported Copper Catalyst. Figure 2 shows scanning electron microscopic/energy-dispersive X-ray spectroscopic images of synthesized copper catalysts with differently dried and calcined alumina supports. In terms of the effect of drying technique, Figure 2a,b,c,f clearly shows that infrared drying resulted in irregularly spherical-shaped particles but with highly uniform sizes (approximately 5 μm with interparticle pore sizes of <1 μm). In contrast, the supports prepared by hot air drying exhibited a large, irregular structure, with intraparticle pore sizes of approximately 10 μm. These
results illustrated that drying technique had a significant impact on the shape and size of pores as well as those of the supports. Infrared drying resulted in better uniformity of copper distribution on the supports when compared with hot air drying, especially at a higher calcination temperature (900 °C) (see Figure 2d,h). Effect of calcination temperature can be seen in Figure 2a–d, which shows the microstructures of the samples prepared by hot air drying and calcination at 600 and 900 °C, respectively. These two catalysts exhibited irregular shapes, with intra-particle pore sizes of 5–10 μm and smaller particles of 1–2 μm dispersed inside the pores and/or near the mouths of the pores. Clearly, the intraparticle pore sizes of Cu–Al_HAD/900 were significantly larger than those of Cu–Al_HAD/600. Moreover, the smaller particles (i.e., copper particles) in the Cu–Al_HAD/900 were more aggregated than those in Cu–Al_HAD/600. Similarly, as is seen in Figure 2e–h, the particle sizes of Cu–Al_IRD/900 were larger; there was less uniformity of the particles in Cu–Al_IRD/900 than in Cu–Al_IRD/600. These results suggested that a higher calcination temperature caused more aggregation of the particles, resulting in larger particle sizes; in other words, catalyst sintering took place. Nevertheless, it is seen that the morphology as well as copper distribution within the catalysts depended more on the drying technique than on the calcination temperature.

Figure 3 shows X-ray diffraction (XRD) patterns of alumina supports (Figure 3a) and those of alumina-supported copper catalysts whose supports were prepared using different drying techniques and at different calcination temperatures (Figure 3b). In Figure 3a, the characteristic peaks of the XRD spectra (2θ = 20.0, 37.6, 39.0, 45.8, 60.0, and 67.3°) corresponded to those of γ-Al2O3.26 The degree of crystallinity of the support prepared (at the same calcination temperature) by hot air drying was higher than that prepared by infrared drying. When comparing the supports prepared using the same drying techniques, increasing the calcination temperature from 600 to 900 °C resulted in a higher degree of crystallinity. In Figure 3b, CuO crystals (2θ = 32.5, 35.5, 38.8, and 48.6°) (PDF 01-080-1916) can be observed. Similarly, the peak intensities of CuO increased with the calcination temperature, indicating higher crystallinity values. These XRD patterns suggested that both drying technique and calcination temperatures have a significant influence on the crystal structure of the supports and catalysts.

The results on BET surface area, average pore size, and pore volume of the alumina supports and alumina-supported copper catalysts are presented in Table 1 and Figure 4. All of the supports were noted to possess pore sizes in the range of 5–20 nm, making them a mesoporous material. BET surface area, pore size, and pore volume of Al_HAD/600 were smaller than those of Al_IRD/600; these results are in good agreement with those discussed in Section 2.1. Similar trends were observed for the samples calcined at 900 °C. After loading copper via the process of impregnation, BET surface areas of all catalysts decreased, while pore sizes increased. This is due to the fact that CuO particles accumulated near the mouths of the pores and/or partially blocked the pores of the supports, thus
reducing the surface area of the impregnated catalysts. On the other hand, CuO particles could create interparticle voids and hence the increased interparticle pore sizes.12 CuO particles could also fill the pores of the supports; this should have resulted in lower pore volumes of the catalysts.27 Nevertheless, it was noted here that the pore volume of Cu−Al_HAD/900 was slightly larger than that of Al_HAD/900. Accordingly to Dumas et al.28 and López-Suárez et al.29 who recommended that copper loading should be 3−6.25 wt % per alumina support surface area of 100 m2/g, Al_HAD/900, which had a surface area of 112 m2/g (the lowest surface area among our tested supports), was supposed to be loaded with 3.4−7 wt % copper. However, because our copper loading was 10%, excess CuO particles could accumulate outside the pores and created new pores in the form of interparticle voids. Note that copper loading above the suitable level would not increase the activity of the catalysts.29

Figure 4 illustrates the N2-sorption isotherms of alumina supports and alumina-supported copper catalysts. The isotherm plots confirm that all of the samples were mesoporous in nature. Interestingly, hysteresis loops of all the samples prepared via infrared drying (see Figure 4a,c) were found to be H1, implying that their pores were cylindrical in shape. In contrast, all of the samples prepared via hot air drying exhibited H2 hysteresis loops, indicating that their pores were of ink-bottle shape and constituted a complex pore structure. Note that pores with an ink-bottle shape are able to serve as barriers for diffusion of reactants and products of the reaction when compared with pores of regular shape.25 Figure 4b,d shows that pore size distributions of the samples prepared by infrared drying were wider than those of the samples prepared by hot air drying.

Peak areas of the samples dried by the same techniques but calcined at different temperatures were different; the samples calcined at 600 °C exhibited larger peak areas than the samples calcined at 900 °C (see Figure 4b,d). These results are consistent with those of the total pore volume reported in Table 1. This implies that increasing the calcination temperature led to collapse of pores and aggregation of smaller particles into larger particles, together resulting in the reduction of the total pore volume.12

The synthesized catalysts were further evaluated using H2-TPR measurement to investigate interactions between copper particles and alumina support; the results are presented in Figure 5 and Table S1. H2-TPR profiles of each catalyst were noted to be in the temperature range of 200−350 °C. The Cu−Al_IRD/600 profile exhibited a single peak at 213 °C,
representing H₂-reduction of the highly dispersed small CuO particles on the support.30 On the other hand, the Cu−Al_IRD/900 profile exhibited one sharp peak at 209 °C and one broad peak at 264 °C; these peaks are attributed to H₂-reduction of the highly dispersed small CuO particles on the support and to the isolated bulk CuO particles.30 The Cu−Al_HAD/600 profile exhibited two sharp peaks at 216 and 233 °C; these peaks are associated with the highly dispersed small CuO particles on the support and to the large CuO particles that had an interaction with alumina, respectively.12 In the case of Cu−Al_HAD/900, three peaks were observed. The peaks at 208 and 307 °C were similar to those belonging to Cu−Al_IRD/900 at 209 and 264 °C, respectively, while the new peak at 238 °C represents the large CuO particles that interacted with the support. It is interesting to note that the H₂-reduction peak of the isolated bulk CuO particles of Cu−Al_HAD/900 exhibited a higher H₂-reduction temperature than that of Cu−Al_IRD/900. This is because the bulk CuO particles of Cu−Al_HAD/900 were larger than those of Cu−Al_IRD/900. These H₂-TPR results are consistent with the microscopic results in Figure 2 in which (i) the catalysts whose alumina supports were prepared via infrared drying exhibited highly dispersed CuO particles on the supports, and (ii) the higher calcination temperature of the support resulted in the aggregation of small particles. The H₂-consumption measurement data also suggested that the suitable temperature for reducing CuO to Cu prior to the reaction is 350 °C.

Figure 5 and Table S1 show NH₃-TPD profiles as well as the number of acid sites of alumina-supported copper catalysts with supports prepared using different drying techniques and at different calcination temperatures. A total of three NH₃ desorption peaks can be observed; the peaks were distributed in the temperature ranges 100−200 °C (denoted as peak α), 200−400 °C (denoted as peak β), and 400−600 °C (denoted as peak γ). α, β, and γ peaks are attributed to weak, medium, and strong acid sites on the catalysts, respectively. Cu−Al_IRD/600 exhibited the highest intensities of both α and β peaks; this was followed in the descending order by Cu−Al_IRD/900, Cu−Al_HAD/600, and Cu−Al_IRD/900. Broad long-tailed γ peak of strong acid sites was observed in the cases of Cu−Al_HAD/600 and Cu−Al_IRD/900, while it was not presented in Cu−Al_IRD/600 and Cu−Al_IRD/900. Keshavarz et al.31 and Sun et al.32 indeed reported that smaller sized catalysts and better dispersion of copper particles on the support resulted in higher concentrations of weak and medium acid sites.

The relationships between acidic properties and catalytic performance of catalysts for methanol dehydration for DME synthesis have previously been studied. It has been reported that the acid sites of weak and medium strength are responsible for the selective formation of DME33,34 while strong acid sites could accelerate the formation of by-products such as CO and CO₂ via the reverse water gas shift reaction (CO₂ + H₂ ↔ CO + H₂O, ΔH = 41.2 kJ mol⁻¹)34 and hence a decrease in DME selectivity.35 These reported results are consistent with our results in Section 2.3. All these results confirmed that infrared drying could prevent the aggregation of copper particles, even when the higher calcination temperature was used. Infrared drying indeed led to the maintenance of weak and medium acid sites, which helped promote the activity of the catalysts for DME production. It is important to note that according to Seo et al.,36 Roy et al.,37 and Bateni and Abel,38 γ-Al₂O₃ only possesses Lewis acid sites. Therefore, the determined acid sites of alumina in our present study should only possess the Lewis acid character.

2.3. Catalytic Performance of Alumina-Supported Copper Catalysts. Copper catalysts whose supports were prepared using the two drying techniques and then calcined at 600 and 900 °C were used to catalyze the synthesis of DME via CO₂ hydrogenation. The results are plotted in terms of CO₂ conversion as well as selectivity of CH₃OH (methanol), CO, and CH₃OCH₃ (DME) as a function of reaction temperature as shown in Figure 7. The reaction was carried out in a fixed bed reactor at reaction temperatures of 240−320 °C, a pressure of 30 atm, and a CO₂:H₂ volume ratio of 1:3.

It is seen in Figure 7a that CO₂ conversions of the catalysts whose supports were calcined at 900 °C were lower than those of the catalysts whose supports were calcined at 600 °C, regardless of the applied drying technique. This is ascribed to the more extensive aggregation (or sintering) of active copper particles at the higher calcination temperature as discussed in Section 2.2. The highest CO₂ conversion was noted to be 34.4%, achieved via the use of Cu−Al_HAD/600 at 320 °C.

As is seen in Figure 7b, an increase in the reaction temperature resulted in the higher CO selectivity. This is because the reverse water gas shift dominated at higher...
temperatures. Cu−Al_HAD/900 yielded the maximum CO selectivity of 93.4% at 320 °C. On the other hand, methanol and DME selectivity values decreased with increasing reaction temperature (see Figure 7c,d, respectively). This is because the reverse water gas shift reaction (eq 2) became more kinetically favored over the hydrogenation reaction to synthesize methanol from CO2 (eq 1) as well as over the dehydration reaction to synthesize DME from methanol (eq 3) at higher temperatures.

Figure 7d illustrates that DME selectivity of Cu−Al_IRD catalysts was significantly higher than that of Cu−Al_HAD catalysts. This is due to the fact that Cu−Al_IRD catalysts had larger pore sizes and higher intensities of weak and medium acid sites than Cu−Al_HAD catalysts (see Table 1). In addition, as mentioned earlier, the pores of Al_IRD catalysts were of cylindrical shape, while those of Al_HAD catalysts were of ink-bottle shape. Diffusion of the products (methanol and DME) out from the catalyst pores of larger sizes and more regular shape was naturally expected to be faster, leading therefore to less decomposition of the products into CO.39,40

Productivities of methanol and DME are plotted in terms of space-time yield as a function of reaction temperature as shown in Figure 8a,b, respectively. As is seen in Figure 8a, Cu−Al_IRD/600 resulted in the highest space-time yield of methanol (59.7 gMeOH kgcat⁻¹ h⁻¹) at 260 °C. The activity of the catalysts for producing methanol can be ordered as follows: Cu−Al_IRD/600 > Cu−Al_HAD/600 > Cu−Al_IRD/900 > Cu−Al_HAD/900. Catalysts whose alumina supports were calcined at 600 °C provided higher space-time yield of methanol than the one whose alumina supports were calcined at 900 °C, regardless of the employed drying techniques. This is because when calcination was conducted at 600 °C, copper particles were better dispersed than doing so at 900 °C.

It is seen in Figure 8b that starting from 240 °C, the space-time yields of DME of all catalysts gradually increased with increasing reaction temperature up to the maximum value of 40.9 gDME kgcat⁻¹ h⁻¹ at 300 °C; the values then rapidly decreased. The space-time yield of DME of the catalysts can be ordered as follows: Cu−Al_IRD/600 > Cu−Al_IRD/900 > Cu−Al_HAD/600 > Cu−Al_HAD/900. The performance of Cu−Al_IRD catalysts to synthesize DME was more promising than that of Cu−Al_HAD catalysts because of the superior pore characteristics of the former as previously illustrated in Figure 7d.

Performance of Cu catalyst with commercial alumina as the support (commercial Cu−Al) was also investigated (see Figure S1). It was observed that DME selectivity of the commercial Cu−Al catalyst was higher than that of our synthesized catalysts. This is because the commercial catalyst had larger pore sizes than our catalysts (see Table 1). However, the commercial catalyst resulted in a lower space-time yields of methanol and DME than Cu−Al_IRD/600 (by about 56.7 and 35.5%, respectively) at the reaction temperature of 300 °C. This is because of the lower surface area of the commercial catalyst, despite its superior dispersion of copper particles (see Figure S2).

The stability of the catalysts was finally examined to determine whether they could potentially be used in industry. The catalysts were evaluated under the same pressure and CO2/H2 feed gas ratio but at the reaction temperature of 280 °C; the reaction was monitored for 24 h. CO2 conversions (Figure 9a) and methanol conversions (Figure 9b) of all catalysts slightly decreased over time, with approximately 10–
Performance in terms of CO2 conversion and methanol conversion of the catalysts whose alumina supports were calcined at 600 °C was superior to that of the catalysts whose alumina supports were calcined at 900 °C because of the better dispersion of copper particles of the former as explained earlier. Interestingly, although CO2 conversions were observed to decrease with time, the space-time yields of DME were remarkably stable over the 24 h period (Figure 9c). This is because methanol and DME molecules are generated at different active sites; the active sites for methanol and DME formations are copper and alumina surfaces, respectively.7 This suggested that DME active sites exhibited excellent stability throughout the 24 h period. Nevertheless, during a longer time-on-stream experiment, DME space-time yield may decrease because of a decrease in methanol as the substantial reactant for the synthesis of DME.

Drying technique of the alumina support had a more significant effect than calcination temperature on the space-time yield of DME. The plots in Figure 9 indicate that the catalytic activity of the Cu-loaded alumina catalyst is highly stable for DME synthesis throughout 24 h, and the Cu–Al IRD/600 catalyst exhibits the highest DME space-time yield.

3. CONCLUSIONS

The effect of using hot air and infrared drying to prepare alumina supports for a copper catalyst was investigated. Infrared drying could shorten the drying time by 75% when compared with hot air drying and at the same time helped lessen shrinkage, resulting in larger pore size, pore volume, and surface area of the supports. Interestingly, infrared drying led to pores of cylindrical shape, while hot air drying resulted in pores of ink-bottle shape; the former technique also resulted in higher intensities of weak and medium acid sites of the catalyst. These results synergistically led to higher activity of the catalyst. In the case of calcination temperature, a higher temperature resulted in a decrease in the surface area of catalyst because of aggregation of particles as well as copper dispersion on the supports. Moreover, the crystalite size of CuO increased with increased calcination temperature. The Cu–Al IRD/600 catalyst exhibited the highest space-time yield of DME (40.9 gDME kgcat⁻¹ h⁻¹) at the reaction temperature of 300 °C, while the highest space-time yield of methanol (59.7 gMeOH kgcat⁻¹ h⁻¹) was achieved at the reaction temperature of 260 °C. Time-on-stream tests of all synthesized catalysts revealed that the catalyst stability for DME synthesis was excellent throughout 24 h of the tests.

4. MATERIALS AND METHODS

4.1. Chemicals. Polyethylene oxide (PEO) (99% purity), propylene oxide (PO) (≥99% purity), aluminum chloride hexahydrate (AlCl3·6H2O) (99% purity), copper (II) nitrate trihydrate (Cu(NO3)2·3H2O) (99% purity), and silicon dioxide (SiO2) (99.5% purity) were obtained from Sigma-Aldrich (St. Louis, MO). γ-Alumina oxide (99.97% purity) was obtained from Alfa Aesar (Ward Hill, MA) and used as the commercial alumina support. Ethanol (99.9% purity) was purchased from RCI Lab-Scan (Bangkok, Thailand). Hydrogen (H2), carbon dioxide (CO2) Helium (He), and argon (Ar) gases (99.999% of purity) were obtained from Thai Special Gas (Pathumthani, Thailand).

4.2. Preparation of Alumina Supports. Porous alumina supports were prepared as per the recommended methods of Tekudome et al.25 PEO (0.08 g) was added into a mixture of ethanol (5.5 mL) and deionized (DI) water (4 mL). The mixture was stirred at room temperature for 1 h. After this, 4.32 g of AlCl3·6H2O was added into the mixture; stirring continued until a clear solution was obtained. Then, 3.75 mL of PO was added into the mixture; the mixture was stirred for 1 min, after which it was kept in a closed system at 40 °C for 24 h. Later, the mixture was divided into two samples. The first sample was dried at 40 °C using a hot-air dryer (Memmert GmbH, UM400, Schwabach, Germany), while the second sample was dried using an infrared dryer at 40 °C; the infrared dryer was the one proposed and tested by Niamnuy et al.44 Both dried samples were calcined under stagnant air at ambient humidity at 600 or 900 °C for 12 h; a heating rate of 10 °C/min was used. Finally, white solids of porous alumina were obtained. Before alumina was used as a catalyst support, each sample were sieved to collect the particles in the size range of 425–600 μm.

4.3. Preparation of Alumina-Supported Copper Catalysts. To create monolayer distribution of copper, Dumas et al.28 and López-Suárez et al.33 suggested that a suitable amount of copper loaded onto an alumina support should depend on the surface area of the support. The recommended copper loading was 3–5 wt % per alumina support surface area of 100 m²/g. Because the BET surface area of our synthesized alumina support varied in the range of 2340 m²/g, the catalysts were prepared by different drying techniques and at different calcination temperatures.

![Figure 8. Influence of reaction temperature on (a) space-time yield of CH3OH and (b) CH3OCH3 of copper catalysts with supports prepared by different drying techniques and at different calcination temperatures.](https://dx.doi.org/10.1021/acsomega.9b03713)
149−290 m²/g, the content of copper loaded onto each support was controlled at 10 wt %.27

Copper loading on both the synthesized and commercial alumina supports was conducted by the incipient wetness impregnation method as follows: 0.419 g of Cu(NO₃)₂·3H₂O was dissolved in 2.5 mL of DI water; the contents were then mixed with 1 g of alumina. After this, the mixture was stirred at 60 °C until dried. The sample was then calcined under stagnant air at ambient humidity at 600 °C for 2 h; a heating rate of 2 °C/min was used. The synthesized copper catalysts, whose supports were dried by hot-air drying (HAD) and infrared drying (IRD) and calcined at 600 and 900 °C, were denoted as Cu−Al_HAD/600, Cu−Al_HAD/900, Cu−Al_IRD/600, and Cu−Al_IRD/900 catalysts, respectively.

4.4. Moisture Content Determination. Moisture content of a sample was gravimetrically determined using AOAC method 984.25.45 About 5 g of the sample was dried at 105 °C until no change in mass was detected.

4.5. Catalyst Characterization. Surface morphology of alumina-supported copper catalysts was assessed with the use of a scanning electron microscope (FEI, Quanta 450, Hillsboro, OR) equipped with energy-dispersive X-ray spectroscopy. The measurements were made at 20 kV. The samples were sputter-coated with gold prior to each measurement.

XRD patterns of alumina supports and alumina-supported copper catalysts were obtained using a diffractometer (JEOL, JDX-3530, Tokyo, Japan) with Cu Kα radiation at 45 kV and 40 mA. The measurements were made at room temperature in a 2θ range of 15−75° with a step size of 0.05°. The diffraction patterns were analyzed according to the guidelines of the Joint Committee on Powder Diffraction Standards.

BET surface area, mesopore size distribution, and pore volume of alumina supports and alumina-supported copper catalysts were determined by N₂-sorption measurement using a gas physisorption analyzer (Quantachrome, Autosorb-1C, Boynton Beach, FL) at −196 °C.

Temperature-programmed reduction (TPR) experiments were conducted using a thermal analyzer (TA Instruments, SDT 2960 Simultaneous DSC−TGA, New Castle, DE). A sample (10 mg) was heated to 350 °C at a heating rate of 10 °C/min under a He atmosphere; the final temperature was maintained for 30 min. Subsequently, the sample was cooled to 100 °C and stabilized. The sample was again heated to 400 °C under flowing 10% (v/v) H₂ (He as a balance gas) at a heating rate of 4 °C/min.

Temperature-programmed desorption using ammonia as a probe molecule (NH₃-TPD) was conducted on a TPDRO apparatus (Thermo Scientific, TPDRO 1100, Waltham, MA) to investigate the acidity of the catalysts. A sample (0.2 g) was pretreated with He flow (30 mL/min) at a heating rate of 10 °C/min until 400 °C was reached; the final temperature was maintained for 60 min. Then, the sample was cooled to 100 °C. Subsequently, 10% (v/v) NH₃ (He as a balance gas) at a flow rate of 30 mL/min was introduced to the sample for 1 h. The NH₃ flow was then disconnected, and the sample was flushed with He at a flow rate of 30 mL/min for 1 h to remove physisorbed NH₃. NH₃ desorption analysis was carried out under the flow of He (30 mL/min) at a heating rate of 10 °C/min from 100 to 600 °C. The intensity of acid sites was
determined from the weight loss because of desorption of NH₃.

4.6. Activity Test of Catalysts. The synthesized alumina-supported copper catalyst (0.5 g) was mixed with 0.5 g of SiO₂, which was used to maintain isothermal conditions in the catalyst bed and packed in a stainless steel tube (316, 3/8 inches ID). H₂ reduction of CuO to Cu(0) was conducted by feeding Ar at 60 mL/min at a reaction temperature of 100 °C and pressure of 1 atm for 1 h. The reaction temperature was then ramped to 350 °C at a heating rate of 2 °C/min. Ar was then switched to H₂ while the final temperature was maintained for 4 h. The reaction temperature was then reduced to 200 °C under the flow of N₂. Subsequently, the system was pressurized to 30 atm using a mixture of CO₂ and H₂ (at a CO₂/H₂ molar ratio of 1:3). The total feeding gas was set at 60 mL/min. The tested reaction temperature was either 240, 260, 280, 300, or 320 °C.

A stability test was carried out at 280 °C and 30 atm for 24 h. All postreactor lines and valves were first heated to 120 °C to avoid condensation of reaction products. The effluent gaseous products were analyzed using gas chromatography. Analysis of H₂, CO, CO₂, and N₂ was performed using gas chromatography (Shimadzu, GC-2014, Kyoto, Japan) equipped with a thermal conductivity detector and a Chromosorb WAW (20% PEG) column. Methanol, DME, and other hydrocarbon products were analyzed using another gas chromatography (Shimadzu, GC-2014, Kyoto, Japan) equipped with a flame ionization detector and a Unibead-C column. Methanol, DME, and other hydrocarbon products were analyzed using another gas chromatography (Shimadzu, GC-8A, Kyoto, Japan) equipped with a thermal conductivity detector and a Chromosorb WAW (20% PEG) column.

Blank reactor experiments (with no catalyst) were run at a reaction temperature of 300 °C to confirm the absence of activity of SiO₂. No reaction products were detected. The activity—selectivity data were calculated from the mass balance from an average of three independent measurements. Selectivity was calculated taking into account the three major products: methanol, CO, and DME; the errors were within ±3% CO₂ conversion. CO₂ conversion, selectivity to methanol, CO, and DME, and space-time yields of methanol and DME are defined as follows

\[
\text{CO₂ conversion} (%) = \frac{\text{moles methanol} + (2 \times \text{moles DME}) + \text{moles CO}}{\text{moles CO₂, in}} \times 100
\]

\[
\text{Methanol selectivity} (%) = \frac{\text{moles methanol}}{\text{moles methanol} + (2 \times \text{moles DME}) + \text{moles CO}} \times 100
\]

\[
\text{CO selectivity} (%) = \frac{\text{moles CO}}{\text{moles methanol} + (2 \times \text{moles DME}) + \text{moles CO}} \times 100
\]

\[
\text{DME selectivity} (%) = \frac{2 \times \text{moles DME}}{\text{moles methanol} + (2 \times \text{moles DME}) + \text{moles CO}} \times 100
\]

Space–time yield of methanol
\[
= \frac{\text{moles methanol}}{\text{moles CO₂, in} \times \text{total amount of catalyst} \times \text{MV}} \times V_{\text{CO}} \times \text{MV}_{\text{methanol}}
\]

Space–time yield of DME
\[
= \frac{\text{moles DME}}{\text{moles CO₂, in} \times \text{total amount of catalyst} \times \text{MV}} \times V_{\text{CO}} \times \text{MV}_{\text{DME}}
\]

where \( V_{\text{CO}} \) is the volumetric flow of CO in cm³/min; \( \text{MW}_{\text{methanol}} \) and \( \text{MW}_{\text{DME}} \) are the molecular weights of methanol and DME in g/mol, respectively; MV is the molar volume of an ideal gas, which is 22,400 cm³/mol at the studied conditions.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03713.

Additional data on surface acidic properties and extents of reduction of alumina-supported copper catalysts as well as morphology and catalytic performance of commercial alumina-supported copper catalysts (PDF)

AUTHOR INFORMATION

Corresponding Author
Chalida Niamnuy — KU-Green Catalysts Group, Department of Chemical Engineering, Faculty of Engineering and Research Network of NANOTEC-KU on NanoCatalysts and NanoMaterials for Sustainable Energy and Environment, Kasetsart University, Bangkok 10900, Thailand; orcid.org/0000-0001-8336-6590

Email: fengcdnj@ku.ac.th; Fax: +66 2 561 4621

Authors
Pawanrat Prapatrakul — KU-Green Catalysts Group, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

Noppadol Panchan — Department of Chemical Engineering, Faculty of Engineering, Mahanakorn University of Technology, Bangkok 10530, Thailand

Anusorn Seubsai — KU-Green Catalysts Group, Department of Chemical Engineering, Faculty of Engineering and Research Network of NANOTEC-KU on NanoCatalysts and NanoMaterials for Sustainable Energy and Environment, Kasetsart University, Bangkok 10900, Thailand; orcid.org/0000-0001-8336-6590

Thongthai Witoon — KU-Green Catalysts Group, Department of Chemical Engineering, Faculty of Engineering and Research Network of NANOTEC-KU on NanoCatalysts and NanoMaterials for Sustainable Energy and Environment, Kasetsart University, Bangkok 10900, Thailand

Sakamon Devahastin — Advanced Food Processing Research Laboratory, Department of Food Engineering, Faculty of Engineering, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand; The Academy of Science, The Royal Society of Thailand, Bangkok 10300, Thailand; orcid.org/0000-0001-9582-1554
Metta Chareonpanich — KU-Green Catalysts Group, Department of Chemical Engineering, Faculty of Engineering and Research Network of NANO TEC-KU on Nano Catalysts and Nano Materials for Sustainable Energy and Environment, Kasetsart University, Bangkok 10900, Thailand

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03713

Notes
The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors express their sincere appreciation to the Kasetsart University Research and Development Institute (KURDI); the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Higher Education, Science, Research and Innovation, Thailand, through its program of Research Network NANOTEC (RNN) for their financial support of this study. Author Devahastin expresses his sincere appreciation to the Thailand Research Fund (TRF) for supporting the study financially through a Senior Research Scholar Grant (grant no. RTA 6180008).

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