

Article

Subscriber access provided by CORNELL UNIVERSITY LIBRARY

Enhanced stability of spatially confined copper nanoparticles in an ordered mesoporous alumina for dimethyl ether synthesis from syngas

Hyungwon Ham, Jihyeon Kim, Sung June Cho, Joon-Hwan Choi, Dong Ju Moon, and Jong Wook Bae ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.6b00882 • Publication Date (Web): 19 Jul 2016 Downloaded from http://pubs.acs.org on July 20, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

ACS Catalysis

Enhanced stability of spatially confined copper nanoparticles in an ordered mesoporous alumina for dimethyl ether synthesis from syngas Hyungwon Ham¹, Jihyeon Kim¹, Sung June Cho², Joon-Hwan Choi³, Dong Ju Moon⁴, Jong Wook Bae^{1,*} ¹School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon, Gyeonggi-do, 440-746, Republic of Korea ²Department of Chemical Engineering, Chonnam National University, Gwangju, 500-757, Republic of Korea ³ Functional Ceramics Department, Korea Institute of Materials Science (KIMS), Changwon, Gyeongnam, 642-831, Republic of Korea ⁴Clean Energy Research Center, Korea Institute of Science and Technology (KIST), 136-791 Seoul, Republic of Korea _____ *Corresponding author (J.W. Bae): Tel.: +82-31-290-7347; Fax: +82-31-290-7272; E-mail address: finejw@skku.edu

Abstract

A spatial confinement effect of copper nanoparticles in an ordered mesoporous gamma-Al₂O₃, which is synthesized by an evaporation induced self-assembly (EISA) method, was investigated to verify the enhanced catalytic activity and stability with a less aggregation of copper crystallites during direct synthesis of dimethyl ether (DME) from syngas. The surface acidity of the mesoporous Al₂O₃ and the metallic copper surface area significantly altered catalytic activity and stability. The ordered mesopore structures of Al₂O₃ were effective to suppress the aggregation of copper nanoparticles even under reductive CO hydrogenation condition through the spatial confinement effect of the ordered mesopores of Al₂O₃ as well as the formation of strongly interacted copper nanoparticles with the mesoporous Al₂O₃ surfaces by partially forming the interfacial CuAl₂O₄ species. The aggregation of copper nanoparticles on the bifunctional Cu/meso-Al₂O₃ having the ordered mesoporous structures was effectively suppressed due to the partial formation of the thermal stable spinel aluminate phases, which can further generate the new acid sites for dehydration of methanol intermediate to DME.

Keywords: Dimethyl ether (DME); ordered mesoporous Al₂O₃; copper nanoparticle; spatial confinement effect; syngas; copper aluminate; bifunctional catalyst.

1. Introduction

Syntheses and applications of mesoporous materials having an ordered mesopore structure with a large specific surface area have been largely reported since the ordered mesoporous materials have superior characteristics such an easy mass transfer and a high dispersion of active metals.^{1,2} Therefore, a lot of bifunctional (or hybrid) catalytic systems containing metallic sites for CO (or CO₂) hydrogenation as well as acid sites for a successive dehydration of alcohols to ethers have been extensively investigated by using the mesoporous materials,³⁻⁶ especially for a direct synthesis of dimethyl ether (DME) from syngas. The active sites of solid acid sites as well as the metallic copper sites haven been well known to be related with a catalytic activity,^{3,6-9} and a catalyst deactivation was strongly attributed to an aggregation of copper nanoparticles with a successive blockage of the acid sites through a well-known sintering process of copper nanoparticles on the bifunctional catalysts.^{6,10-15}

In addition, DME having a similar chemical property with liquefied petroleum gas (LPG) has been attracted as an alternative clean fuel due to its lower emission of NO_x and SO_x pollutants than conventional diesel fuel.^{16,17} Compared to the commercialized two-step synthesis of DME via methanol synthesis by CO (or CO₂) hydrogenation, one step synthesis of DME form syngas on the bifunctional catalysts has some advantages by effectively operating even at a low H₂/CO molar ratio and a high CO₂ concentration. These characters are mainly attributed to the intrinsically high activity for a water-gas shift reaction by overcoming a thermodynamic equilibrium limitation on the hybridized Cu-ZnO-Al₂O₃/solid acid catalysts with solid-acid components of zeolites, γ -Al₂O₃ or silica-alumina and so on.^{3-5,8,18,19} Among the various solid acid catalysts, Al₂O₃ has been widely reported for a dehydration reaction of methanol to DME due to its proper acid site strength and amount with

a less hydrocarbon formation compared to zeolites.^{10,11,20,21} However, some disadvantages of the soli-acid Al_2O_3 have been known to possess a relatively small amount of acid sites and a hydrophilic character, which is prone to deactivate the bifunctional catalysts by a facile water adsorption and a significant aggregation of the supported copper nanoparticles.^{3,6,12,13,15,22}

Even though the preparation methods of the ordered mesoporous materials and their applications for various catalytic reactions have been largely reported,²³⁻²⁵ the bifunctional catalyst possessing copper nanoparticles supported on a regular mesoporous Al_2O_3 having a narrow pore size distribution has not been well investigated till now as far as we know. In the present study, some positive effects of ordered mesoporous γ -Al₂O₃ prepared by evaporation induced self-assembly (EISA) method are tentatively verified with respect to spatial confinement effect of a small amount of copper nanoparticles in an ordered mesoporous Al_2O_3 with the help of newly formed spinel copper aluminate phases. Finally, the enhanced catalytic stability for a direct synthesis of DME from syngas is mainly explained through a spatial confinement effect with a less aggregation of copper nanoparticles.

2. Experimental Details

2.1. Catalyst preparation and activity measurement

A ordered mesoporous Al_2O_3 was synthesized by EISA method as precisely reported by other investigators²³⁻²⁵ by mixing Pluronic P123 (MW = 5800, EO₂₀PO₇₀EO₂₀, Sigma-Aldrich) dissolved in 60 mL of ethanol solvent with aluminum isopropoxide (Al(OC₃H₇)₃, Junsei) solution dissolved in another 60 mL of ethanol with HNO₃ after a vigorous stirring of two solutions for 2 h separately. The above solution mixtures were stirred completely for 6 h at an ambient temperature followed by drying at 60 °C in an oven for 2 days to evaporate a residual

Page 5 of 44

ACS Catalysis

solvent completely. The as-prepared light-yellow powder was further annealed at 400 °C for 4 h and an additional thermal treatment was carried out to prepare solid-acid Al₂O₃ catalyst at different calcination temperatures. The as-prepared solid-acid Al₂O₃ are denoted as mesoAl and mesoAl(HT) at the calcination temperatures of 800 and 900 °C for 1 h, respectively. For comparison, a commercial Al₂O₃ (Puralox γ -Al₂O₃ with a purity over 99.9% with a main impurity of SiO₂ (below 150 ppm) from Sasol) was also used as solid-acid catalyst after thermal annealing at 800 °C for 1 h, and it is denoted as Al. On the as-prepared solid-acid Al_2O_3 , copper nitrate precursor was subsequently impregnated by incipient wetness impregnation method with a fixed 10wt% copper based on the total weight of a bifunctional Cu/Al₂O₃ catalyst. The catalyst was dried again at 70 °C for overnight, and it was subsequently calcined at 350 °C for 3 h under air environment. The final as-prepared bifunctional catalysts are denoted as the Cu/mesoAl, and Cu/mesoAl(HT), and the Cu/Al represents the bifunctional catalyst containing 10 wt% copper on the commercial Al₂O₃. In order to get rid of an internal mass transport problem in the mesopores, the solid acid Al₂O₃ having a particle size of $5 - 30 \,\mu\text{m}$ was used, where the size is known to show a trivial effect for an internal mass transport limitation.^{26,27} The morphologies and particle size distributions of the Al₂O₃ supports with magnified images are displayed in supporting Figure S1 characterized by scanning electron microscopy (SEM) analysis, and the Al₂O₃ particles are found to be irregular sphere shapes especially on the commercial Al₂O₃.

A catalytic activity was measured using a fixed-bed tubular flow reactor having an outer diameter of 9.5 mm and an inner diameter of 7 mm. Before the activity test, the bifunctional Cu/Al_2O_3 catalyst was previously reduced at 300 °C for 5 h under a flow of 5vol% H₂ balanced with N₂. A direct DME synthesis from syngas was performed at the following

reaction conditions of P = 5.0 MPa, T = 250 °C, and space velocity of 2000 L/(kg_{cat}·h) using the syngas having a molar ratio of H₂/CO/N₂ = 63:31.5:5.5 with 0.4 g catalyst. To get rid of an initial activity loss by a fast ramping of temperature at a high pressure, reaction pressure was previously adjusted by filling it with syngas at room temperature and the temperature was raised up to reaction temperature with a ramping rate of 0.5 °C/min. The products were in-situ analyzed by gas chromatography (YL6100 GC, Younglin) equipped with flame ionization detector (FID) connected with Plot-Q capillary column to analyze methanol, DME, and hydrocarbons and the GC equipped with thermal conductivity detector (TCD) connected with Carboxen-1000 packed column for measuring the effluent gases of CO, H₂, N₂, CO₂. The CO conversion (X_{CO}) and selectivity of products (S_i) was calculated based on the following equations:

$$X_{CO} \text{ (mol \%)} = 1 - \frac{CO_{out}}{CO_{in}} \times 100$$
$$S_{i} \text{ (mol \%)} = \frac{C_{i}}{CO_{in} - CO_{out}} \times 100$$

where, CO_{out} , CO_{in} and C_i stand for moles of the inlet and outlet CO and moles of the product i component (i.e. $i = CO_2$, CH₃OH, DME, and C₁ - C₂ hydrocarbons). The conversion of CO and selectivity of products were calculated using the data at steady-state after reaction of 25 h on stream on the bifunctional Cu/Al₂O₃ catalysts.

2.2. Catalyst characterization

N₂ adsorption-desorption analysis was applied to measure Brunauer-Emmett-Teller (BET) surface area, pore volume, and Barrett-Joyner-Halenda (BJH) pore size distribution from the desorption branch on the as-prepared Al₂O₃ supports and bifunctional Cu/Al₂O₃ catalysts

using TRISTAR-3000 (Micromeritics) working at -196 °C. BET surface area was estimated using the data in a relative pressure (P/P_0) of 0.03 to 0.2, and pore volume was calculated at a relative pressure of 0.99 from the desorption branch.

Temperature programmed reduction analysis with H₂ (TPR) was carried out using BELCAT-M instrument to characterize the reducibility of the fresh bifunctional Cu/Al₂O₃ catalyst in the temperature range of 100 - 500 °C at a heating rate of 10 °C/min. Before TPR analysis, the fresh Cu/Al₂O₃ catalyst was pretreated at 300 °C for 1 h at a ramping rate of 10 °C/min under Ar environment with a flow rate of 30 mL/min to remove any contaminant and adsorbed water. After the pretreatment, a reduction gas of 5vol%H₂ balanced with Ar was introduced at a flow rate of 30 mL/min, and the hydrogen consumption was measured by TCD after passing through water trap. In addition, the TPR patterns of the fresh bifunctional Cu/Al₂O₃ catalysts after a stepwise reduction-oxidation treatment at the respective 300 and 350 °C for 5 h were also measured to verify the aggregation of supported copper crystallites and the their interaction with the support during reduction step. Furthermore, additional TPR experiment with a different ramping rate of 2 °C/min on the Cu/mesoAl was carried out to confirm a homogeneous distribution of copper crystallites as well. Temperature programmed desorption of NH_3 (NH_3 -TPD) analysis was carried out in the temperature range of 100 - 600 °C at a ramping rate of 10 °C/min to characterize the strengths and amounts of acid sites on the fresh Al₂O₃ supports and Cu/Al₂O₃ catalysts before and after reduction using BELCAT-M instrument. Before NH₃-TPD analysis, the sample was pretreated at 300 °C for 1 h under He flow for the Al₂O₃ supports and 5vol%H₂ balanced with Ar for Cu/Al₂O₃ catalysts. After the pretreatment, pure NH₃ gas was adsorbed for 1 h at a flow rate of 30 mL/min. After the adsorption of NH₃, the sample was flushed under He flow for 1 h at 100 °C to remove the

physisorbed NH₃. The NH₃-TPD pattern was successively measured by TCD and mass spectrometer (YL6900 MS, Younglin) for the fragment species of m/z = 16, 18 and 44.

The surface area (m²/g_{cat}) of metallic copper crystallites was measured by N₂O titration using AutoChem II 2920 instrument. Before the N₂O analysis, the sample was reduced at 300 °C for 5 h using a reducing gas of 10vol%H₂ balanced with N₂, and it was flushed under He flow at 100 °C for 1 h. The consumption of N₂O on the reduced sample was analyzed by measuring the formed amount of N₂ and that of unreacted N₂O with TCD equipped with a Porapak Q packed column. The surface area of metallic copper crystallites was further calculated based on the value of the generated amount of N₂ using an equation of N₂O + 2Cu = Cu₂O + N₂. A metallic copper surface area was also calculated by assuming 1.46 x 10¹⁹ copper atoms/m² with a molar stoichiometry of 2 for number of copper atom exposed on the surface per N₂O molecule.²⁸

Powder X-ray diffraction (XRD) analysis was used to identify the crystalline phases and crystallite sizes of the supported copper nanoparticles on the bifunctional Cu/Al₂O₃ catalysts using D8 ADVANCE instrument equipped with Cu-K α radiation having a wavenumber of 0.15406 nm. The characteristic XRD patterns of copper species and alumina were collected in the range of 10 - 80° at a scanning rate of 4°/min. The crystallite size of CuO and metallic copper nanoparticles were calculated by using Scherrer equation with the most intense characteristic peak of copper species at $2\theta = 35.4^{\circ}$ for CuO on the fresh Cu/Al₂O₃ catalysts and $2\theta = 43.3^{\circ}$ for metallic copper species on the used ones. The ordered mesoporous structures of the as-synthesized Al₂O₃ were also confirmed by small angle X-ray scattering (SAXS) analysis using ANTON PAAR instrument with Cu-K α radiation. For the SAXS

of $q = 4\pi \sin(\theta/\lambda)$, where λ is the wavelength of X-ray of 0.15406 nm. The Al₂O₃ sample was exposed to X-ray for 1 min and the scattered X-ray was gathered on a detecting film.

Transmission electron microscopy (TEM) analysis was further carried out to clarify the changes of the surface morphology and local crystallite size distribution of the supported copper nanoparticles on the solid-acid Al₂O₃ surfaces for the fresh and used Cu/Al and Cu/mesoAl(HT) catalysts using TECNAI G2 instrument operating at 200 kV.

The oxidation states and surface concentrations of copper and aluminum species on the fresh and used Cu/Al₂O₃ catalyst were characterized using X-ray photoelectron spectroscopy (XPS) analysis with a VG Multilab 2000 (ThermoVG Scientific) instrument. The Al K α monochromatized line (1486.8eV) with a resolution of 0.05 eV was adopted for X-ray source to analyze the Al 2p and Cu 2p_{3/2}. The binding energy (BE) of copper and aluminum was adjusted with a reference BE of C 1s (284.6 eV). The relative oxidation states of copper nanoparticles were measured using the intensity ratio of Cu and CuO species by comparing the value of I_{Cu}/I_{CuO} (i.e., the integrated area ratio of the deconvoluted Cu and CuO peak). In addition, the outermost surface concentrations of the copper species were characterized using the intensity ratio of I_{Cu}/I_{Al} of the integrated area of Cu 2p3/2 and Al 2p peak, respectively.

To verify the copper phases on the Cu/Al₂O₃ catalysts before and after reaction after air exposure, X-ray absorption fine structure (XAFS) analysis of Cu K-edge (8979 eV) was performed at the 7D1 beam line in Pohang Light Source (PLS). The beam line was equipped with a Si(111) monochromator and ionization chambers for measuring transmitted beam intensities. The powder sample was attached on the tape and positioned between two Ohken ionization chambers filled with nitrogen gas for measuring the incident and transmitted X-ray intensity. A simultaneous measurement of the absorption spectra of the metallic Cu foil, CuO,

 Cu_2O and $CuAl_2O_4$ were also carried out, and normalization and XAFS analysis were performed using an Athena graphical interface program.²⁹ XANES (X-ray absorption nearedge structure) originating from an excitation of core electron to a vacant d-orbital of the copper metal, which reflects the d-orbital electron vacancy (denoted as white line area (A_{WL})) of the Cu/Al₂O₃ catalysts and EXAFS (extended X-ray absorption fine structure) data were also analyzed to calculate coordination number of Cu-Cu (denoted as CN(Cu-Cu)) and Cu-O (denoted as CN(Cu-O)) as well as to calculate radius (R/Å) of Cu-O on the fresh and Cu-Cu on the used Cu/Al₂O₃ catalysts.

3. Results and discussion

3.1. Physicochemical and reduction properties of the Cu/Al₂O₃ catalysts

The ordered mesoporous structures of the solid-acid Al_2O_3 and Cu/Al_2O_3 catalysts were confirmed by N₂ sorption and SAXS analysis. The pore size distribution patterns and N₂ adsorption-desorption isotherms are displayed in **Figure 1** and supporting **Figure S2**, respectively. The average ordered mesopore sizes on the mesoAl supports were found to be 6.0 nm as summarized in **Table 1**. The mesopore size was decreased to 4.0 nm on the mesoAl(HT) with an increase of calcination temperature up to 900 °C due to a possible mesopore shrinkage of main Al_2O_3 frameworks at a high temperature thermal treatment condition.^{30,31} The formation of the regular Al_2O_3 mesopores was also supported by observing a typical type IV adsorption-desorption isotherms on the supports as well as bifunctional catalysts as shown in supporting **Figure S2**. The type IV isotherm with H₁ type hysteresis can be generally observed on the mesoporous materials, and the hysteresis loop at a lower relative pressure on the Cu/mesoAl than that of the Cu/Al suggests the formation of relatively smaller

pores with slightly disordered cylindrical mesopore channels.^{1,2} On the contrary, the average pore size on the commercial Al₂O₃ was found to be a larger size of 9.5 nm with a broad pore size distribution. As shown in supporting Figure S3, the well-formation of the ordered mesopores on the Al₂O₃ supports was further verified by SAXS analysis which showed the characteristic diffraction peaks of the 2D hexagonal mesopore structures assigned to the plane of (100) reflection.²³⁻²⁵ Therefore, an observed lower surface area of 150 m^2/g and larger pore volume of 0.47 cm³/g on the commercial Al₂O₃ compared with those of 204 - 253 m²/g and 0.37 - 0.43 cm³/g on the ordered mesoporous Al₂O₃ seem to be attributed to an irregular pore size distribution. Interestingly, the ordered mesopore structures of the mesoporous Al_2O_3 was preserved even after 10wt% copper impregnation by revealing a decreased surface area in the range of 173 - 180 m^2/g with a decreased average pore size of 3.8 nm due to a preferential deposition of copper nanoparticles inside of mesoporous Al₂O₃ surfaces having an average pore diameter of ~ 6 nm by stretching them inside of Al₂O₃ mesopores.³⁰ These advantageous physicochemical properties such as large surface area with pore volume and ordered mesoporous Al₂O₃ structures were clearly observed on the Cu/mesoAl and Cu/mesoAl(HT). These characteristics seem to be responsible for an enhanced catalytic activity and stability on the Cu/mesoAl and Cu/mesoAl(HT) compared with the Cu/Al. It is also attributed to the formation of active crystalline planes by forming active copper defect sites^{32,33} through a spatial confinement effect and a newly formed strong metal-support interaction possibly.

The surface area of metallic copper species plays an important role for CO hydrogenation to methanol, and a large surface area of metallic copper by an easy reducibility of CuO is responsible for a high catalytic activity for methanol synthesis.^{12,34,35} In addition, the strong interactions of copper crystallites with solid-acid Al₂O₃ sites are also important to suppress

the aggregation of copper nanoparticles during the reaction.^{6,10,14,31} The reduction behavior and proper metal-support interaction between copper nanoparticles and solid-acid Al₂O₃ were measured by TPR experiment, and the reduction patterns of the fresh Cu/Al₂O₃ catalysts (solid line) are shown in Figure 2 with the reduction patterns on the Cu/Al_2O_3 catalysts after successive reduction-calcination treatment (dashed line) as well. Two distinctive reduction peaks were clearly observed on the fresh Cu/Al at around 145 °C and 221 °C, which can be attributed to the reduction of heterogeneously dispersed copper oxides on the Al₂O₃ surfaces and the reduction of bulk copper oxides, respectively.^{19,36} However, only one large reduction peak with a Gaussian pattern was observed on the Cu/mesoAl and Cu/mesoAl(HT) at around 216 and 185 °C, respectively. This observation suggests the homogeneous size distribution of copper nanoparticles inside of the mesoporous Al_2O_3 . The observed Gaussian pattern of the TPR peak on the Cu/mesoAl and Cu/mesoAl(HT) compared to the Cu/Al suggests the homogeneous distribution of the supported cupper nanoparticles. In addition, the observed Gaussian reduction patterns at a different ramping rate of 2 °C/min during TPR experiment strongly suggest a homogeneous distribution of copper nanoparticles as shown in supporting Figure S4. The reduction peak shift to a lower temperature on the Cu/mesoAl(HT) compared to the Cu/mesoAl revealed the decreased interaction between copper nanoparticles and solid acid Al_2O_3 since a thermal treatment at high temperature of the Al_2O_3 can induce a crystallization as well as dehydration of Al₂O₃ surfaces, which can largely decrease an interaction of copper nanoparticles with the acidic Al₂O₃ surfaces.³⁷

As summarized in supporting **Table S1**, a larger amount of H_2 consumption during TPR experiment, which was related with the well dispersion of copper nanoparticles, was also found on the Cu/mesoAl and Cu/mesoAl(HT) with the values around 0.87 - 0.95 mmolH₂/g

than that of Cu/Al with the value of $0.80 \text{ mmolH}_2/\text{g}$. The roles of the acidic Al₂O₃ surfaces for a different interaction of the supported copper nanoparticles were further verified by measuring the crystallite size of the copper precursor of Cu₂(OH)₃NO₃ before calcination. The XRD patterns and crystallite sizes of copper precursor are shown in supporting Figure **S5.** The size of the copper precursor before calcination was found to be somewhat larger on the Cu/mesoAl(HT) with a value of 52 nm than that of the Cu/mesoAl with 46 nm due to the decreased metal-support interaction. However, the copper precursor size is much larger on the Cu/Al with a value of 76 nm. It suggests that the relatively smaller copper crystallites seems to be effectively confined on the Cu/mesoAl and Cu/mesoAl(HT) through a strong metalsupport interaction (SMSI) between the copper nanoparticles and acidic surface of Al_2O_3 . In addition, the TPR patterns of the reduced Cu/Al₂O₃ catalysts at 300 °C with subsequently reoxidized Cu/Al₂O₃ catalysts were obtained (dashed line) as shown in **Figure 2**. The second reduction patterns on the Cu/Al after reduction-oxidation treatment showed a similar two characteristic reduction peaks due to its intrinsic nature of the heterogeneous size distribution of the supported copper nanoparticles by easily forming aggregated copper crystallites.^{6,10,14,15,31} However, similar reduction patterns on the Cu/mesoAl and Cu/mesoAl(HT) even after reduction-oxidation treatment were observed by approaching the maximum reduction temperature at around 185 °C from the respective temperature of 216 and 165 °C on the fresh ones. This observation suggests that the thermally stable copper nanoparticles can be preserved by forming a new strong interaction in the ordered mesopores of Al₂O₃ with the help of a spatial confinement effect. This seems to be possibly attributed to the partial formation of spinel $CuAl_2O_4$ species, which can generate the much stronger interaction between the copper nanoparticles and Al_2O_3 .

Interestingly, a partial formation of the spinel copper aluminate species seems to be more favorable on the Cu/meosAl catalysts due to an observed lower H₂ consumption and a larger amount of acid sites on the mesoporous Al₂O₃. The SMSI effect was possibly enhanced through the spatial confinement effect of the supported copper nanoparticles in the ordered mesopores of Al_2O_3 having a size of 4 - 6 nm, which probably resulted in changing the electronic property and crystalline planes of the supported copper nanoparticles.^{32,33} Therefore, the degree of reduction of the Cu/Al₂O₃ catalysts was calculated by using H₂ consumption below 300 °C divided by a total theoretical amount of H₂ consumption and the results are summarized in **Table 1**. The degree of reduction was found to be around 29.1, 32.2, and 34.5 % on the Cu/Al, Cu/mesoAl, and Cu/mesoAl(HT), respectively. The lower reduction degree on the Cu/Al seems to be attributed to a bimodal size distribution of the strongly interacted copper nanoparticles on the commercial Al₂O₃. However, the larger degree of reduction and the Gaussian reduction pattern even after the reduction-oxidation treatment on the Cu/mesoAl and Cu/mesoAl(HT) seem to be attributed to a strong interaction of copper nanoparticles with the acid sites of the ordered Al₂O₃ structures. In addition, the SMSI effect on the Cu/mesoAl and Cu/mesoAl(HT) can be attributed to the partial surface decoration of the metallic copper with aluminum species, 38 which was also supported by TPR patterns by shifting to a high temperature on the Cu/mesoAl(HT) than that of the Cu/Al. A higher reducibility of the copper nanoparticles and partial formation of thermally stable copper aluminates on the Cu/mesoAl and Cu/mesoAl(HT) can be beneficial for suppressing active copper aggregation during the reaction with the help of the SMSI and spatial confinement effect, which was clearly verified by XAFS analysis as well.³³

3.2. Surface acidity of the Cu/Al₂O₃ catalysts to the dispersion of copper nanoparticles

The amounts and strengths of the acid sites on the Cu/Al₂O₃ catalysts are important for the high DME selectivity through a successive dehydration reaction of methanol formed by CO hydrogenation.^{3,8,39} A large number of the weak acid sites on the solid acid γ -Al₂O₃ or zeolites have been known to be closely related with a high dispersion of metal crystallites as well. In addition, a high byproduct formation like light hydrocarbons can be also attributed to the presence of strong acid sites through an subsequent dehydration or decomposition of DME or methanol.^{7,9,10} As shown in supporting Figure S6, the desorption peak below 300 °C in NH₃-TPD can be assigned to the only desorption of NH_3 (m/z =16) and others are assigned to water desorption from the bifunctional Cu/Al₂O₃ surfaces. This behavior was confirmed by a simultaneous analysis with mass spectrometer, and the adsorbed amount of NH₃ was only assigned to the deconvoluted area with a Gaussian pattern below 300 °C of the NH₃-TPD peaks. The summaries of NH₃-TPD analysis on the solid acid Al₂O₃ and fresh Cu/Al₂O₃ catalysts are presented in **Table 1**. The amount of acid sites on the solid acid Al_2O_3 themselves were found to be 0.11, 0.29 and 0.24 mmolNH₃/g on the commercial Al_2O_3 , mesoAl and mesoAl(HT), respectively. In general, large acid sites of the supporting materials are responsible for a high dispersion of the supported metals through the selective adsorption of metal ions.^{30,40-42} Interestingly, total acid sites on the fresh Cu/Al₂O₃ catalysts were significantly increased to 0.13, 0.45 and 0.42 on the Cu/Al, Cu/mesoAl and Cu/mesoAl(HT), respectively as summarized in **Table 1**. These increases seem to be attributed to a newly formed copper aluminate species, especially on the Cu/mesoAl and Cu/mesoAl(HT). Even though the acidic sites on the reduced Co/Al₂O₃ catalysts were decreased as summarized in supporting Table S1, the acid sites on the reduced Cu/mesoAl and Cu/mesoAl(HT) still

showed a larger amount than that of the Cu/Al.

The large amount of acid sites on the Cu/mesoAl and Cu/meaoAl(HT) can increase the CO conversion though a consecutive dehydration of methanol to DME, which seems to be crucial for a lower aggregation of the supported copper nanoparticles through a strong metal-support interaction on the acidic sites as well. To confirm the acid site strengths, the acid sites were deconvoluted to weak and medium acid sites as summarized in supporting Table S1. The amount of weak acid sites below the desorption temperature of 200 °C (assigned to W as shown in Table S1) was found to be larger on the mesoAl compared to the medium acid sites (assigned to M as shown in **Table S1**) with the respective values of 0.23 and 0.06mmolNH₃/g on the mesoAl. Interestingly, the weak and medium acid sites on the Cu/mesoAl were dramatically changed to the respective values of 0.20 and 0.25 mmolNH $_3$ /g. This observation can be attributed to the formation of an interfacial copper aluminate species by generating new acid sites with a medium strength. A large amount of acid sites with a medium strength was found on the Cu/mesoAl(HT). Therefore, the acid sites on the ordered mesoporous Al₂O₃ are prone to interact with the copper nanoparticles strongly by forming much smaller nanoparticles than that of the Cu/Al. This newly formed strong interaction is probably attributed to the interfacial formation of copper aluminate on the acid sites of the ordered mesoporous Al₂O₃, which is responsible for a less aggregation due to a simultaneous spatial confinement effect in the ordered mesopores of Al₂O₃. However, on the commercial Al_2O_3 , the surface acidity was decreased due to the blockage of Al_2O_3 pores by forming larger copper nanoparticles during the reduction of reaction. The enhanced thermal stability of copper nanoparticles on the Cu/mesoAl and Cu/mesoAl(HT) seems to be attributed to the preserved acid sites by simultaneously generating strongly interacted copper nanoparticles

with the partial formation of spinel copper aluminate.

From the results of N₂O titration as summarized in **Table 1**, the observed somewhat larger surface area of metallic copper with the values of $5.9 - 7.1 \text{ m}^2/g_{cat}$ on the fresh Cu/mesoAl and Cu/mesoAl(HT) than that of 5.5 m^2/g_{cat} on the Cu/Al can be possibly attributed to the well-dispersed copper nanoparticles on the acidic sites of the ordered mesoporous Al₂O₃ due to the presence of a larger amount of acid sites.⁴⁰⁻⁴³ These properties can largely enhance the catalytic activity and stability by increasing CO hydrogenation activity to methanol and a successive dehydration activity to DME.¹¹ This observation was also supported by XRD analysis as shown in Figure 3(A) and supporting Table S1. The fresh Cu/Al showed a larger crystallite size of CuO of \sim 50 nm, which was calculated from the most intense characteristic diffraction peak of CuO. However, the Cu/mesoAl and Cu/mesoAl(HT) showed the much smaller sizes not to be detected from XRD analysis. In general, the surface area of metallic copper has been reported to be inversely correlated with the copper crystalline size.⁴³ Compared to a significantly different crystallite size, the observed insignificant surface area variation of metallic copper seems to be attributed to the heterogeneous crystallite size distribution on the Cu/Al. The thermal stability of copper nanoparticles in the ordered mesoporous Al₂O₃ can be largely enhanced even under reaction due to the strong interaction of copper nanoparticles with acid sites as reported in our previous researches^{6,10,30,40-42} and the spatial confinement effect.

3.3. Catalytic performance of the Cu/Al₂O₃ catalysts

The CO conversion and product distribution for direct DME synthesis from syngas on the bifunctional Cu/Al_2O_3 are summarized in **Table 2** and the CO conversion with time on stream

for 40 h is shown in Figure 4. A similar CO conversion of 11.5% and DME selectivity of 76.1% (based on the total hydrocarbons and oxygenates formed without CO_2) were observed on the Cu/mesoAl(HT) and the respective values of 9.6 and 78.5% on the Cu/mesoAl. These values are much larger than the Cu/Al with the respective values of 5.7 and 67.9%. The observed relatively low CO conversion on the Cu/mesoAl with a high stability was attributed to a lower content of copper with 10 wt% on the ordered mesoporous alumina compared with a high concentration of copper (above 70 wt%Cu) on hybridized Cu-ZnO-Al₂O₃/solid acid catalysts with CO conversion above 40% and a fast deactivation nature as reported from our previous works.^{6,11,14} The extent of CO₂ formation on the Cu/Al₂O₃ catalysts was proportional to CO conversion due to the proportional water-gas shift reaction activity with water formed during methanol dehydration to DME. The observed high catalytic activity on the Cu/mesoAl and Cu/mesoAl(HT) was attributed to the ordered mesoporous structures of the Al₂O₃ with the highly dispersed copper nanoparticles on a large amount of acid sites. As shown in **Table** 1, a fast methanol dehydration rate to DME,^{33,44,45} which was formed by CO hydrogenation on the active metallic copper sites, seems to be responsible for a high CO conversion on the Cu/mesoAl and Cu/meaoAl(HT) which has large metallic copper sites and acid sites. The observed higher DME selectivity of 78.5% on the Cu/mesoAl than the Cu/mesoAl(HT) of 76.1 % seems to be also attributed to a larger amount of newly formed medium-strength acid sites (M), which can be possibly originated from copper aluminate formation as summarized in supporting **Table S1** and section 3.2. The high selectivity of byproducts (mainly methane) on the Cu/Al of 17.8% compared with 6.3% on the Cu/mesoAl can be attributed to the large crystallite sizes of metallic copper, which are active sites for methanation of CO or decomposition of intermediates such as methanol or DME possibly.^{6,14,31,46,47} The catalytic

ACS Catalysis

stability in terms of CO conversion and reaction rate for 40 h on stream was found to be much higher on the Cu/mesoAl and Cu/mesoAl(HT) than the Cu/Al as shown in Figure 4 and supporting **Figure S7**. The observed long induction period to approach steady-state conversion for ~ 12 h on all Cu/Al₂O₃ catalysts was mainly attributed to a slow ramping rate of reaction temperature for minimizing an initial deactivation. However, selectivity to DME with time on stream as shown in supporting Figure S8 revealed a fast approach to steadystate value. In addition, the reference catalyst of Cu/mesoAl(w/o P123) which was prepared through a similar method of the Cu/mesoAl without using P123 (shown in supporting Table **S2**) also showed a fast deactivation like the Cu/Al due to an irregular pore structure formation on the Cu/mesoAl(w/o P123). CO conversion was decreased from 7.8% at 12 h on stream to 5.6% at steady-state for 40 h reaction on the Cu/mesoAl(w/o P123), however, CO conversion was slightly increased from 8.0% at 12 h on stream to 9.6% at steady-state for 40 h reaction on the Cu/mesoAl. Therefore, it seems to be mainly attributed to the stabilization of the active sites of metallic copper nanoparticles with a suppressed aggregation through the formation of strongly interacted copper crystallites by possibly forming copper aluminate on the acid sites.

The positive confinement effect of the homogeneously distributed copper crystallites in the ordered mesoporous Al_2O_3 with the possible generation of new acid sites was also verified by comparing the catalytic activity of methanol dehydration to DME on the Cu/mesoAl and Cu/mesoAl(HT) at the reaction condition of T = 250 °C and P = 0.1 MPa. As summarized in supporting **Table S3**, a slightly higher methanol conversion and DME selectivity were observed on the Cu/mesoAl with the respective values of 27.9 and 67.3% compared to the Cu/mesoAl(HT) with the respective values of 24.9 and 64.8%. The observed higher methanol

conversion and DME selectivity with a lower formation of methyl formate and methyl acetate on the Cu/mesoAl than Cu/mesoAl(HT) can be attributed to a fast dehydration of methanol to DME on the largely exposed acid sites including newly formed acid sites and metallic copper crystallites.^{6,10,11} This observation also suggests that the spatially confined copper nanoparticles with smaller crystallite sizes on the Cu/mesoAl increases the exposed acid sites compared with Cu/mesoAl(HT). In addition, the strongly interacted copper crystallites with a high metal surface area on the acidic Al₂O₃ surfaces (confirmed by TPR and XRD) can be responsible for a further dehydrogenation to methyl formate.⁴⁸ The catalytic stability of the copper nanoparticles on the bifunctional Cu/Al₂O₃ catalysts has been known to be largely affected by the extent of sintering phenomena of the supported copper nanoparticles and the simultaneous changes of the acid site density during the reaction.^{6,10,11,14,31,46,47}

To further verify the intrinsic activity on the Cu/Al₂O₃ catalysts, the reaction rate defined as the reacted CO mmol/(g_{cat} ·h) and turnover frequency (TOF) defined as the reacted CO molecules/(surface copper metal atom·s) using the metallic copper surface area of the used catalysts are summarized in **Table 2**. The reaction rates of 2.69, and 3.24 mmol/(g_{cat} ·h) were found on the Cu/mesoAl and Cu/meaoAl(HT) and these values are two times larger than the Cu/Al of 1.60 mmol/(g_{cat} ·h). However, TOF values on all Cu/Al₂O₃ catalysts showed a small variation in the range of 0.0049 - 0.0063 molecule/(surface copper metal atom·s) due to the structural sensitive characters in the range of a lower value of (surface area of copper) x (amount of acid site) for the direct DME synthesis reaction from syngas.^{6,10,11} In general, the reaction rates on the Cu/Al₂O₃ catalysts have been known to be strongly affected by the total number of the defect sites and types of metallic copper crystallite facets^{32,38} as well as by the interfaces between the copper crystallites and solid acid Al₂O₃ surfaces.⁴⁹ The thermal

stability of copper nanoparticles inside of the mesoporous Al_2O_3 seems to change the catalytic activity significantly, and the spatial confinement effect of the copper nanoparticles inside of the ordered Al_2O_3 mesopores can largely enhance the thermal stability by partially forming stable copper aluminate during the oxidation and reaction period.

3.4. Thermal stability of copper nanoparticle on the mesoporous Cu/Al₂O₃ catalysts

To further verify the thermal stability of the copper nanoparticles in the ordered mesoporous Al₂O₃, the XRD, N₂O titration, XPS and TEM analysis on the fresh and used catalysts were carried out. XRD patterns of the fresh Cu/Al₂O₃ catalysts showed characteristic diffraction peaks of CuO at $2\theta = 35.4$, 38.6, 48.6, 53.4, 58.2, and 61.3 (JCPDS No: 048-1548) and γ -Al₂O₃ at $2\theta = 19.6$, 32.2, 37.1, 39.7, 46.0, 60.8, and 66.9° (JCPDS No: 00-010-0425). Even though the CuO phase was not detected on the Cu/mesoAl and Cu/mesoAl(HT) due to highly dispersed CuO nanoparticles inside of ordered Al₂O₃ mesopores possibly, the crystallite size of CuO on the fresh Cu/Al was found to be around 48.2 nm as calculated by the FWHM value from Figure 3(A). The impregnated copper nanoparticles on the ordered mesoporous Al_2O_3 with a pore size of 4 - 6 nm seem to be well dispersed with a smaller size than that of mesopores on the Cu/mesoAl and Cu/mesoAl(HT). However, new characteristic diffraction peaks of the metallic copper at $2\theta = 43.3$, 50.3, and 74.1 (JCPDS No: 04-0836) were clearly observed on the used Cu/Al_2O_3 catalysts as shown in Figure 3(B). The calculated crystallite sizes of the metallic copper nanoparticles with the help of Scherrer equation using the most intense diffraction peak at $2\theta = 43.3^{\circ}$ were found to be around 88.7 and 5.2 nm on the used Cu/Al and Cu/mesoAl(HT), respectively. This observation also supports a less aggregation of copper nanoparticles inside of the ordered mesoporous Al₂O₃, especially on the Cu/mesoAl

without showing any characteristic diffraction peaks of metallic copper. As summarized in **Table 1**, the surface area variation on the fresh and used catalysts were found to be from 7.1 to 5.3 m²/g_{cat} on the Cu/mesoAl(HT) and 5.9 to 4.9 m²/g_{cat} on the Cu/mesoAl and from 5.5 to 3.8 m²/g_{cat} on the Cu/Al. The small variation of the surface area of metallic copper measured by N₂O titration on the fresh and used Cu/mesoAl strongly suggests the suppressed aggregation of copper nanoparticles on the ordered mesoporous Al₂O₃. We believe that a less aggregation of copper nanoparticles inside of the ordered mesoporous Al₂O₃ can be attributed to the spatial confinement effect as well as the formation of the strongly interacted copper nanoparticles by forming copper aluminate species, which are preferential on the Cu/mesoAl.

The oxidation sates of the copper nanoparticles and Al₂O₃ with their surface concentrations were measured by XPS analysis on the fresh and used Cu/Al₂O₃ catalysts. The summarized surface concentrations of I_{Cu}/I_{CuO} and I_{Cu}/I_{A1} and BEs of Cu and Al species are presented in **Table 1**, supporting **Table S1** and **Figure S9**. The intensity ratios of the I_{Cu}/I_{CuO} for comparing the oxidation states of copper nanoparticles was calculated by deconvoluting Cu $2p_{3/2}$ peak appearing at 932 - 935 eV on the used Cu/Al₂O₃ catalysts. In addition, the surface ratios of I_{Cu}/I_{A1} were also calculated using the integrated area of Cu $2p_{3/2}$ divided by that of Al 2p on the fresh and used Cu/Al₂O₃ catalysts after correcting the area using atomic sensitivity factors of Cu and Al species.⁵⁰ The BEs of copper species were found in the range of 934.7 – 935.4 eV on the fresh Cu/Al₂O₃ catalysts without significant deviations, which corresponds to the CuO phase of the supported copper crystallites mainly. However, BEs of copper species on the used Cu/Al₂O₃ catalysts shifted to a lower BE in the range of 932.8 – 932.9 eV, which suggests the presence of partially reduced CuO species as summarized in supporting **Table S1** and **Figure S9**. Interestingly, somewhat higher binding energy of aluminum species was

observed at the BE of 76.18 eV on the fresh Cu/Al and that of 74.59 eV on the used Cu/Al compared with those of the Cu/mseoAl of the respective values of 74.36 and 74.44 eV, which corresponds to gamma-phase Al_2O_3 .⁵⁰ The observed higher BE of Al 2p on the Cu/Al may be attributed to a large number of defect sites on the commercial Al₂O₃ surfaces by strongly interacting with CuO species. As shown in supporting Figure S9, the observed similar BEs of aluminum species with a large peak intensity on the used Cu/mesoAl seem to be attributed to a preservation of the stable gamma-phase Al₂O₃ before and after reaction. We believe that the higher BE of aluminum species on the Cu/Al can be also responsible for the higher byproduct formation through the further reaction of methanol (or DME) to hydrocarbons. As shown in Table 1, the I_{Cu}/I_{CuO} ratios can be also related with a strong metal-support interaction between copper nanoparticles and Al₂O₃. The I_{Cu}/I_{CuO} ratios were found to be smaller on the Cu/mesoAl(HT) with the value of 1.97 and larger values between 2.46 and 2.52 on the Cu/Al and Cu/mesoAl, respectively. A higher oxidation state and lower I_{Cu}/I_{CuO} ratio of copper nanoparticles on the Cu/mesoAl(HT) than those of the Cu/mesoAl seems to be attributed to the preferential aggregation of copper nanoparticles as confirmed by XRD analysis. In addition, the strong interaction of copper nanoparticles with the acidic Al_2O_3 sites can form a thermally stable copper aluminate species as well, which was confirmed by TPR experiments. In addition, it was also attributed to the abundant formation of partially reduced Cu₂O surfaces confirmed by XAFS analysis during the reduction and reaction period possibly. Furthermore, the variation of surface concentrations of the copper species was verified by comparing the ratio of I_{Cu}/I_{Al} on the fresh and used Cu/Al₂O₃ catalysts as summarized in **Table 1.** Although the surface concentration of copper species on the fresh Cu/mesoAl(HT) was found to be a higher than other Cu/Al_2O_3 catalysts from the value of 0.087, the copper

nanoparticles seem to be redispersed in the inside of mesoporous Al_2O_3 judged from the decreased intensity ratio of 0.056 after reaction on the Cu/mesoAl(HT). This observation can be surely attributed to a spatial confinement effect of copper nanoparticles with a suppressed aggregation by forming strong metal-support interaction, and the phenomena were similar on the Cu/mesoAl as well by changing from 0.066 to 0.077 of the ratio of I_{Cu}/I_{Al} during the reaction. However, the more significant aggregation of the copper nanoparticles was observed on the Cu/Al by showing the increased intensity ratio of I_{Cu}/I_{Al} from 0.068 to 0.077 during the direct synthesis reaction of DME from syngas without less effects of the spatial confinement.

The proposed spatial confinement effect inside of the mesoporous Al_2O_3 were also verified by TEM analyses on the Cu/mesoAl(HT) and Cu/Al before and after reaction for 40 h. The TEM images are displayed in **Figure 5** with the large scale images in the inset figure of Cu/mesoAl(HT) and supporting **Figure S10** for the Cu/Al. The copper nanoparticles with the crystallite sizes of ~ 5 nm were well dispersed in the ordered mesoporous Al_2O_3 surfaces on the fresh Cu/mesoAl(HT), and the size of copper crystallites was not significantly altered even after the reaction for 40 h as shown in **Figure 5**. However, the larger copper crystallites above the average crystallite size of ~50 nm were observed on the fresh Cu/Al, and the size of copper particles significantly increased to the much larger crystallite size above ~80 nm as shown in supporting **Figure S10**. The significant aggregation of the supported copper nanoparticles on the Cu/Al₂O₃ catalytic systems has been generally observed on an irregular pore size distribution having a larger pores.^{6,10,11} Therefore, the suppressed aggregation of the copper nanoparticles inside of the ordered mesoporous Al₂O₃, especially on the Cu/mesoAl compared to the Cu/Al, can be attributed to a spatial confinement effect of the ordered mesoporous Al₂O₃, which are strongly interacted with the acid sites on the Al₂O₃ by partially

generating the copper aluminate species (confirmed by TPR and XPS experiments).

3.5. Enhanced catalytic stability through an interfacial copper aluminate formation

The verification of a newly formed SMSI and a thermally stable copper aluminate formation between the well-dispersed copper nanoparticles and the ordered mesoporous Al₂O₃ surfaces were further verified by XAFS analysis of the fresh and used Cu/Al₂O₃ catalysts. As shown in Figure 6 and supporting Figure S11, XANES spectra and their first derivatives showed that the main phase of copper species on the fresh Cu/Al_2O_3 was found to be the CuO phase confirmed by the characteristic absorption energy at around 8985 and 8997 eV without significant differences. As summarized in **Table 1** and supporting **Table S4**, the CNs of the Cu-O on the fresh Cu/Al_2O_3 catalysts were found to be around 3.4 - 3.6 and the white line areas (A_{WL}) were found to be similar on the Cu/mesoAl and Cu/mesoAl(HT) with the respective values of 7.29 and 7.74 compared to the Cu/mesoAl with the value of 6.51. As shown in supporting Figure S12 and Table S4, the linear combination fittings (LCF) of the fresh and used Cu/Al₂O₃ catalysts were also performed to verify the possible compositions of copper species. These fitting results showed that the fresh Cu/Al_2O_3 catalysts mainly have the phases of the CuO and CuAl₂O₄ with the respective compositions of 0.41 and 0.59 on the Cu/Al, 0.10 and 0.90 on the Cu/mesoAl and 0.09 and 0.91 on the Cu/mesoAl(HT). This result suggests that the Cu/mesoAl and Cu/mesoAl(HT) possess much stronger interactions between copper crystallites and the Al₂O₃ surfaces by preferentially forming the copper aluminate compared to the fresh Cu/Al. However, the compositions of the copper aluminate after reaction were dramatically decreased from 0.59 to 0.40, 0.90 to 0.70, and 0.91 to 0.60 on the used Cu/Al, Cu/mesoAl, and Cu/mesoAl(HT), respectively. This result strongly

suggests the partial reduction of copper aluminate to metallic copper during the reaction. Nevertheless, the Cu/mesoAl and Cu/mesoAl(HT) still had an abundant copper aluminate species even after reaction by simultaneously containing CuO, Cu₂O, and CuAl₂O₄ species. However, the metallic copper species was the main phase on the used Cu/Al due to a severe aggregation of copper nanoparticles, which was more preferential species due to the larger copper crystallite formation on the used Cu/Al. These characterization results strongly suggests that the ordered mesoporous Al_2O_3 can sufficiently inhibit a complete reduction of the confined copper nanoparticles to the metallic copper due to a newly formed strong interaction with ordered mesoporous Al_2O_3 surfaces by preferentially forming the copper aluminate species which still having acidic properties. Therefore, the enhanced catalytic stability seems to be attributed to the less aggregation of copper nanoparticles during the reaction on the Cu/mesoAl and Cu/mesoAl(HT) compared with the Cu/Al. In addition, the larger white line area (A_{WL}) on the used Cu/mesoAl and Cu/mesoAl(HT) with the respective values of 6.92 and 6.24 compared to the Cu/Al with the value of 5.85 supports the thermally stability of the newly formed copper aluminate. The k³-weighted $\chi(k)$ EXAFS spectra of the Cu/Al₂O₃ catalysts before and after reaction are displayed in Figure 7 and the results are summarized in Table 1 with supporting Table S4. Two main peaks at around 1.0 - 1.5 and 2.0 - 2.6 Å were originated from first oxygen coordination shell (Cu-O) around the absorbing atoms and the second Cu-Cu contribution through the two-step diffusion-limited reduction of $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$, respectively.^{51,52} The observed different radial distances of the Cu/Al with Cu/mesoAl and Cu/mesoAl(HT) as shown in Figure 7 were mainly caused by the difficult reduction degree of the copper oxides due to a strong confinement effect. The second peak of Cu-Cu on the Cu/Al was the main peak originated from the metal copper phase.

However, the second peak of Cu-Cu on the Cu/mesoAl and Cu/mesoAl(HT) was mainly attributed to the copper oxides such as CuAl₂O₄ species, since the peak position was similar with the CuAl₂O₄ reference. These results strongly support that the degrees of SMSI are in the order of Cu/mesoAl > Cu/mesoAl(HT) > Cu/Al, which are well corresponding with the results of TPR, XRD, XPS and TEM analysis. Therefore, the first derivatives of the copper K-edge XANES spectra and the Fourier transform of k^3 -weighted $\chi(k)$ EXAFS spectra as shown in Figure 7 and Figure S11 clearly revealed the formation of the CuAl₂O₄ phase on the used Cu/mesoAl and Cu/mesoAl(HT). Furthermore, the CNs of Cu-O on the used Cu/mesoAl and Cu/mesoAl(HT) were found to be around 3.0 - 3.3 without significant differences from fresh ones, except for the Cu/Al with a large variation from 3.6 to 2.0 due to a severe aggregation of copper nanoparticles instead of the thermally stable copper aluminate formation. The CNs of the Cu-Cu on the used Cu/Al₂O₃ catalysts also showed a similar trend, i.e., the CN of Cu-Cu on the used Cu/Al showed a larger value of 3.5, however, smaller CNs of the Cu-Cu with the values of 0.9 - 1.2 were observed on the used Cu/mesoAl and Cu/mesoAl(HT), which strongly suggest the stable maintenance of copper aluminate species even after reaction. From the above XAFS analyses, the aggregation of copper nanoparticles during the reaction seems to be less favorable than the formation of copper aluminate on the Cu/mesoAl and Cu/mesoAl(HT) compared to the Cu/Al due to a spatial confinement effect of copper nanoparticles in the ordered mesoporous Al₂O₃, which seem be mainly responsible for the largely enhanced catalytic stability and activity. Therefore, we believe that the formation of the interfacial $CuAl_2O_4$ layers between copper oxide (mainly Cu_2O) crystallites and acid sites of the ordered mesoporous Al_2O_3 as schematically proposed in Figure 5 (TEM analysis) seems to be the main reason for the enhanced thermal stability of copper crystallites and

catalytic activity by suppressing a thermal aggregation of copper nanoparticles inside of the ordered mesopores, especially on the bifunctional Cu/mesoAl and Cu/mesoAl(HT).

In summary, the supported copper nanoparticles on the bifunctional Cu/Al₂O₃ having an ordered mesopore structures with an average pore size of ~ 4 nm can effectively suppress the catalyst deactivation by forming the thermally stable copper nanoparticles inside of the ordered mesopores through an efficient spatial confinement effect of copper crystallites in the ordered mesoporous Al₂O₃ frameworks. The strongly interacted copper nanoparticles with the solid acid mesoporous Al₂O₃ surfaces can also form interfacial CuAl₂O₄ layers partially, and it can stabilize the copper nanoparticles through SMSI even under the reaction. These positive characteristics of the ordered mesoporous Al₂O₃ can enhance the catalyst stability and DME selectivity as well. Therefore, the proposed novel catalyst preparation method by forming thermally stable and spatially confined copper nanoparticles inside of an ordered mesoporous Al₂O₃ can be applied for preparing an efficient stable hybridized catalytic system of a direct DME synthesis from syngas without significant catalyst deactivation.

4. Conclusions

The direct synthesis of DME from syngas using the bifunctional Cu/Al₂O₃ catalyst, where the copper nanoparticles were impregnated on the ordered mesoporous solid acid Al₂O₃, was investigated to elucidate the spatial confinement effect of the ordered mesoporous Al₂O₃ for a significant suppression of the copper nanoparticle aggregation during the reaction. The supported copper nanoparticles in the ordered mesoporous Al₂O₃ were well-dispersed by partially forming the interfacial CuAl₂O₄ species, which is thermally stable species by providing new acid sites as well. The bifunctional Cu/mesoAl catalyst having a regular pore Page 29 of 44

ACS Catalysis

size of ~ 4 nm showed the homogeneous dispersion of the copper nanoparticles by forming thermally stable copper nanoparticles inside of the ordered mesoporous Al_2O_3 structures through the spatial confinement effect. The strongly interacted copper nanoparticles with the acid sites of the ordered mesoporous Al_2O_3 surfaces was newly formed through the formation of the interfacial CuAl₂O₄ layers, and it also provides some efficient acid sites for the methanol dehydration to DME. The highly dispersed copper nanoparticles with strong interactions on the abundant acid sites of the ordered mesoporous Al_2O_3 largely enhanced the catalyst stability and DME selectivity as well.

Acknowledgments

The authors acknowledge the financial support from the National Research Foundation of Korea (NRF) grant funded by the Korea government (NRF-2014R1A1A2A16055557, NRF-2015M3D3A1A01064898 and NRF-2016M3D3A1A01913253). This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) with Project numbers of 20132010201750 of the Ministry of Knowledge Economy (MKE) of Korea. This work was also financially supported by an institutional program grant (2E26570-16-037) from the Korean Institute of Science and Technology (KIST) and by Fundamental Research Program of the Korea Institute of Materials Science (PNK4310).

Supporting information

The supporting information contains additional characterization results of the SEM images of Al and mesoAl (**Figure S1**), N₂ adsorption-desorption patterns (**Figure S2**), small angle X-ray scattering (SAXS) patterns (**Figure S3**), H₂-TPR profiles at a different ramping rate of 2

and 10 °C/min (Figure S4), X-ray diffraction (XRD) patterns of the as-prepared Cu/Al₂O₃ catalysts (Figure S5), NH₃-TPD patterns measured by TCD and mass spectrometer (Figure S6), reaction rate of CO conversion to products (Figure S7), DME selectivity (Figure S8), XPS spectra of Cu 2p_{3/2} and Al 2p (Figure S9), TEM images of the fresh and used Cu/Al catalysts (Figure S10), copper K-edge XANES spectra (Figure S11) and linear combination fittings (LCF) of the used Cu/Al₂O₃ catalysts (Figure S12). In addition, the summaries of various characterizations with XAFS analysis and dehydration activity on the Cu/mesoAl are respectively included in Table S1, Table S2, Table S3 and Table S4. This information is available free of charge via the Internet at http://pubs.acs.org.

References

- (1) LeoFanti, G.; Padovan, M.; Tozzola, G.; Venturelli, B. Catal. Today 1998, 41, 207-219.
- (2) Dumeignil, F.; Sato, K.; Imamura, M.; Matsubayashi, N.; Payen, E.; Shimida, H. Appl. Catal. A: Gen. 2003, 241, 319-329.
- (3) Akarmazyan, S. S.; Panagiotopoulou, P.; Kambolis, A.; Papadopoulou, C.; Kondarides, D.
 I. *Appl. Catal. B: Environ.* 2014, *145*, 136-148.
- (4) Vishwanathan, V.; Jun, K. W.; Kim, J. W.; Roh, H. S. Appl. Catal. A: Gen. 2004, 276, 251-255.
- (5) Xu, M.; Lunsfor, J. H.; Goodman, D. W.; Bhattacharyya, A. Appl. Catal. A: Gen. 1997, 149, 289-301.
- (6) Jung, J. W.; Lee, Y. J.; Um, S. H.; Yoo, P. J.; Lee, D. H.; Jun, K. W.; Bae, J. W. Appl. Catal. B: Environ. 2012, 126, 1-8.
- (7) Aguayo, A. T.; Gayubo, A. G.; Vivance, R.; Olazar, M.; Bilbao, J. Appl. Catal. A: Gen.

2005, 283, 197-207.

- (8) Li, Z.; Li, J.; Yang, C.; Wu, J. J. Nat. Gas Chem. 2012, 21, 360-365.
- (9) Li, Z.; Li, J.; Dai, M.; Liu, Y.; Han, D.; Wu, J. Fuel 2014, 121, 173-177.
- (10) Lee, Y. J.; Jung, M. H.; Lee, J. B.; Kwang, K. E.; Roh, H. S.; Suh, Y. W.; Bae, J. W. *Catal. Today* **2014**, *228*, 175-182.
- (11) Bae, J. W.; Kang, S. H.; Lee, Y. J.; Jun, K. W. J. Ind. Eng. Chem. 2009, 15, 566-572.
- (12) Sun, Q.; Zhang, Y. L.; Chen, H. Y.; Deng, J. F.; Wu, D. ; Chen, S. Y. J. Catal. 1997, 167, 92-105.
- (13) Mao, D.; Yang, W.; Xia, J.; Zhang, B.; Song, Q.; Chen, Q. J. Catal. 2005, 230, 140-149.
- (14) Bae, J. W.; Kang, S. H.; Lee, Y. J.; Jun, K. W. Appl. Catal. B: Environ. 2009, 90, 426-435.
- (15) Kim, A. R.; Lee, B.; Park, M. J.; Moon, D. J.; Bae, J. W. *Catal. Commun.* **2012**, *19*, 66-69.
- (16) Semelsberger, T. A.; Borup, R. L.; Greene, H. L. J. Power Sources 2006, 156, 497-511.
- (17) Hu, J.; Wang, Y.; Cao, C.; Elliott, D. C.; Stevens, D. J.; White, J. F. Ind. Eng. Chem. Res.
 2005, 44, 1722-1727.
- (18) Kim, J. H.; Park, M. J.; Kim, S. J.; Joo, O. S.; Jung, K. D. Appl. Catal. A: Gen. 2004, 264, 37-41.
- (19) Zhang, Y.; Li, D.; Zhang, Y.; Cao, Y.; Zhang, S.; Wang, K.; Ding, F.; Wu, J. Catal.*Commun.* 2014, 55, 49-52.
- (20) San, X.; Zhang, Y.; Shen, W.; Tsubaki, N. Energy Fuels 2009, 23, 2843-2844.
- (21) Jin, D.; Zhu, B.; Hou, Z.; Fei, J.; Lou, H.; Zheng, X. Fuel 2007, 86, 2707-2713.
- (22) Sung, D. M.; Kim, Y. H.; Park, E. D.; Yie, J. E. Catal. Commun. 2012, 20, 63-67.

2	
3	
4	
5	
6	
7	
0	
0	
9	_
1	0
1	1
1	2
1	3
1	4
1	5
1	6
1	0
1	1
1	8
1	9
2	0
2	1
2	2
2	2
2	1
2	4
2	5
2	6
2	7
2	8
2	9
3	0
3	1
2	ว
ວ າ	2 2
ა ი	S د
3	4
3	5
3	6
3	7
3	8
3	9
1	0 0
4	1
4	1
4	2
4	3
4	4
4	5
4	6
4	7
4	8
1	ă
+ F	0 0
о г	4
5	
5	2
5	3
5	4
5	5
5	6
5	7
5	י פ
5	0
с С	3
6	υ

(23) Yuan, Q.; Yin, A. X.; Luo, C.; Sun, L. D.; Zhang, Y. W.; Duan, W. T.; Liu, H. C.; Yan, C.

- H. J. Am. Chem. Soc. 2008, 130, 3465-3472.
- (24) Wang, X.; Pan, D.; Xu, Q.; He, M.; Chen, S.; Yu, F.; Li, R. Mater. Lett. 2014, 135, 35-38.
- (25) Zhao, X.; Zheng, Y.; Zheng, Y.; Zhan, Y.; Zheng, X. RSC Adv. 2014, 4, 12497-12505.

(26) Larmier, K.; Chizallet, C.; Cadran, N.; Maury, S.; Abboud, J.; Lamic-Humblot, A. F.; Marceau, E.; Lauron-Pernot, H. *ACS Catal.* **2015**, *5*, 4423-4437.

(27) Madon, R. J.; Boudart, M. Ind. Eng. Chem. Fundam. 1982, 21, 438-447.

(28) Jensen, J. R.; Johannessen, T.; Livbjerg, H. Appl. Catal. A: Gen. 2004, 266, 117-122.

(29) Ravel, B.; Newville, M. J. Synchrotron Radiat. 2005, 12, 537-541.

(30) Woo, M. H.; Cho, J. M.; Jun, K. W.; Lee, Y. J.; Bae, J. W. *ChemCatChem* **2015**, *7*, 1460-1469.

(31) Bae, J. W.; Potdar, H. S.; Kang, S. H.; Jun, K. W. Energy Fuels 2008, 22, 223-230.

(32) Zhao, D. Y.; Huo, Q. S.; Feng, J. L.; Chmelka, B. F.; Melosh, N.; Fredrikson, G. H.;Stucky, G. D. *Science* 1998, *279*, 548–552.

(33) Jiang, H.; Bongard, H.; Schmidt, W.; Schuth, F. *Micropor. Mesopor. Mater.* 2012, *164*, 3-8.

(34) Gao, P.; Li, F.; Zhao, N.; Xiao, F.; Wei, W.; Zhong, L.; Sun, Y. *Appl. Catal. A: Gen.* **2013**, *468*, 442-452.

- (35) Burch, R.; Golunski, S. E.; Spencer, M. S. Catal. Lett. 1990, 5, 55-60.
- (36) Agrell, J.; Boutonnet, M.; Cabrera, I. M.; Fierro, J. L. G. *Appl. Catal. A: Gen.* 2003, 253, 201-211.

(37) Garbowski, E.; Primet, M. J. Chem. Soc. Commun. 1991, 11-12.

(38) Behrens, M.; Studt, F.; Kasatkin, I.; Kuhl, S.; Havecker, M.; Pedersen, F. A.; Zander, S.;

1	
2 3	
4	Girgsdies, F.; Kurr, P.; Kniep, B. L.; Tovar, M.; Fischer, R. W.; Norskov, J. K.; Schlogl, R.
5	
0 7	Science 2012, 336, 893-897.
8	(39) Arena E: Dario R: Parmaliana A Annl Catal A: Gan 1998 170 127-137
9	(37) Alena, F., Dallo, K., Fallianana, A. Appl. Calal. A. Oen. 1376, 170, 127-137.
10 11	(40) Lee, H. Y.; Kim, A. R.; Park, M. J.; Jo, J. M.; Lee, D. H.; Bae, J. W. Chem, Eng. J. 2015.
12	(\cdot)
13	280, 771-781.
14	
15 16	(41) Cho, J. M.; Ahn, C. I.; Pang, C.; Bae, J. W. Catal. Sci. Technol. 2015, 5, 3525-3535.
10	(42) K-L T. K H. M. K. T. Lin, D. D I. W. ACC Critical 2014, 4, 1054, 1000
18	(42) Kon, I.; Koo, H. M.; Yu, I.; Lim, B.; Bae, J. W. ACS Catal. 2014 , <i>4</i> , 1054-1060.
19	(43) Kasatkin I. Kurr P. Knien B. Trunschke A. Schlogl R Angew Chem Int Ed 2007
20	(15) Rusukin, I., Run, I., Rinep, D., Truisenke, R., Seniogi, R. Ingew. Chem. Int. Ed. 2007,
21	119, 7465-7468.
23	
24	(44) Moradi, G.; Ahmadpour, J.; Nazari, M.; Yaripour, F. Ind. Eng. Chem. Res. 2008, 47,
25 26	
20	7672-7679.
28	(15) Khoshbin R · Haghighi M Catal Sci Technol 2014 1 1779-1792
29	(45) Knoshom, K., Magnigin, W. Calal. Sci. Technol. 2014, 4, 1779-1792.
30 31	(46) Aguayo, A. T.; Erena, J.; Sierra, I.; Olazar, M.; Bilbao, J. Catal. Today 2005, 106, 265-
32	
33	270.
34	
35 36	(47) Mao, D.; Yang, W.; Xia, J.; Zhang, B.; Lu, G. J. Mol. Catal. A: Chem. 2006, 250, 138-
37	144
38	144.
39	(48) Lu Z. Gao D. Yin H. Wang A. Liu S. J. Ind. Eng. Chem. 2015, 31, 301-308
40 41	(10) Lu, L., Cuo, D., Thi, H., Wang, H., Liu, C.C. Hui, Ling. Choine 2010 , 21, 301 300.
42	(49) Liu, X. M.; Yan, Z. F.; Lu, G. Q. Chin. J. Chem. 2006, 24, 172-176.
43	
44	(50) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. Handbook of X-ray
45 46	
47	Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and
48	Interpretation of XPS Data Physical Electronics Division Perkin-Elmer Corn. 1995
49	interpretation of XI'S Data, I hysical Electronics Division, I erkin-Eliner Corp., 1995.
50 51	(51) Kim, J. Y.; Rodriguez, J. A.; Hanson, J. C.; Frenkel, A. I.; Lee, P. L. J. Am. Chem. Soc.
52	
53	2003 , <i>125</i> , 10684-10692.
54	
55 56	
57	33
58	
59	
60	

(52) Cassinelli, W. H.; Martins, L.; Passos, A. R.; Pulcinelli, S. H.; Rochet, A.; Briois, V.;Santilli, C. V. *ChemCatChem* 2015, *7*, 1668-1677.

Figure Captions

Figure 1. Pore size distribution of the (A) Al₂O₃ supports and (B) bifunctional Cu/Al₂O₃ catalysts

Figure 2. TPR profiles of the fresh bifunctional Cu/Al₂O₃ catalysts with first reduction (solid

line) and a subsequent oxidation at 350 °C followed by second reduction (dashed line)

Figure 3. X-ray diffraction (XRD) patterns of the (A) fresh bifunctional Cu/Al₂O₃ and (B)

used bifunctional Cu/Al₂O₃ catalysts

Figure 4. CO conversion with time on stream on the bifunctional Cu/Al₂O₃ catalysts

Figure 5. TEM images of the (A) fresh Cu/mesoAl(HT) and (B) used Cu/mesoAl(HT)

Figure 6. Copper K-edge XANES spectra of the (A) fresh Cu/mesoAl and (B) used Cu/mesoAl with the reference samples of Cu, Cu₂O, CuO, and CuAl₂O₄

Figure 7. Fourier transform of k^3 weighted (k) EXAFS spectra of the (A) fresh Cu/mesoAl₂O₃ and (B) used Cu/mesoAl₂O₃ with the reference sample spectra of Cu, Cu₂O, CuO, and CuAl₂O₄ species.

ACS Catalysis

Notation	N ₂ sorption (support/catalyst) ^a			Amount of acid sites (mmol NH ₃ /g) ^b		Surface area of Cu	Degree of	XPS		XAFS (before/after) ^g		
	Sg (m²/g)	Vp (cm ³ /g)	Dp (nm)	Support	Fresh	(before/after) $(m^2/g_{cat})^c$	reduction (%) ^d	I _{Cu} /I _{CuO} (after) ^e	I_{Cu}/I_{Al} ratio (before/after) ^f	\mathbf{A}_{WL}	CN (Cu-O)	CN (Cu-Cu)
Cu/Al	150/117	0.47/0.41	9.5/10.6	0.11	0.13	5.5/3.8	29.1	2.46	0.068/0.077	6.51/5.85	3.6/2.0	-/3.4
Cu/mesoAl	253/180	0.43/0.23	6.0/3.8	0.29	0.45	5.9/4.9	32.2	2.52	0.066/0.057	7.29/6.92	3.5/3.0	-/1.2
Cu/mesoAl(HT)	204/173	0.37/0.22	4.0/3.8	0.24	0.42	7.1/5.3	34.5	1.97	0.087/0.056	7.74/6.24	3.4/3.3	-/0.9

Table 1. The physicochemical properties, surface are and concentration of the active copper on the bifunctional Cu/Al₂O₃ catalysts

^aSg stands for surface area (m²/g), Vp for pore volume (cm³/g) and Dp for average pore diameter (nm) of support and Cu impregnated catalyst. ^bThe amounts of acid sites were measured by NH₃-TPD on the supports themselves and fresh Cu/Al₂O₃ catalysts with the weak acid sites calculated from the deconvoluted peak below around 300 °C.

^cThe surface area of metallic copper was evaluated through N₂O titration method on the fresh and used Cu/Al₂O₃ catalyst.

^dThe degree of reduction of copper oxides was calculated using an equation of (measured amount of H₂ below 300 °C)/(theoretical amount of hydrogen consumption of the catalyst)*100 from TPR experiment with a theoretical amount of H₂ consumption of 1.57 mmol/g_{cat}.

^eThe intensity ratio of I_{Cu}/I_{CuO} was calculated from the Cu $2p_{3/2}$ on the used bifunctional Cu/Al₂O₃ catalysts by deconvoluting the Cu $2p_{3/2}$ at around 932 - 935 eV.

^fThe surface ratio of I_{Cu}/I_{Al} was calculated using the area of Cu $2p_{3/2}$ divided by that of Al 2p on the fresh and used Cu/Al₂O₃ catalyst.

^gThe X-ray adsorption fine structure (XAFS) analysis at the Cu K-edge (8979 eV) was performed at the 7D1 beam line of the Pohang Light Source (PLS), and the relative white line area (denoted as A_{WL}) was calculated from XANES regions on the fresh and used Co/Al₂O₃ catalysts. The coordination number of Cu-O (denoted as CN (Cu-O)) was calculated on the fresh Cu/Al₂O₃ catalysts and that of Cu-Cu (denoted as CN (Cu-Cu)) were also calculated on the on the used bifunctional Cu/Al₂O₃ catalysts as well.

Notation	Rate ^a	TOF^{a} (x10 ²)	CO conversion (mol%)	CO conversion to CO ₂ (mol%)	Product distribution (mol%)			
					Methanol	DME	BP ^b	
Cu/Al	1.60	0.49	5.7	1.9	14.3	67.9	17.8	
Cu/mesoAl	2.69	0.63	9.6	2.4	15.2	78.5	6.3	
Cu/mesoAl(HT)	3.24	0.61	11.5	3.5	18.9	76.1	5.0	

Table 2. Catalytic activity on the bifunctional Cu/Al₂O₃ catalysts

^aThe reaction rate was defined as the reacted CO mmol/(g_{cat} ·h), and the turnover frequency (TOF) for the reacted CO molecules/(surface copper metal atom s) using the metallic surface area of copper of the used catalysts.

^bBP stands for the byproducts, which are mainly hydrocarbon species such as C_1 - C_2 paraffin, at the reaction conditions of P = 5.0 MPa, T = 250 °C, and space velocity = 2000 L/(kg_{cat} h) using the syngas having a molar ratio of H₂/CO = 2 with 0.4 g catalyst.



Figure 1. Pore size distribution of the (A) Al₂O₃ supports and (B) bifunctional Cu/Al₂O₃ catalysts



Figure 2. TPR profiles of the fresh bifunctional Cu/Al₂O₃ catalysts with first reduction (solid line) and a subsequent oxidation at 350 °C followed by second reduction (dashed line)





Figure 3. X-ray diffraction (XRD) patterns of the (A) fresh bifunctional Cu/Al₂O₃ and (B) used bifunctional Cu/Al₂O₃ catalysts



Figure 4. CO conversion with time on stream on the bifunctional Cu/Al₂O₃ catalysts



Figure 5. TEM images of the (A) fresh Cu/mesoAl(HT) and (B) used Cu/mesoAl(HT)





Figure 6. Copper K-edge XANES spectra of the (A) fresh and (B) used Cu/Al₂O₃ catalysts with the reference samples of Cu, Cu₂O, CuO, and CuAl₂O₄



Figure 7. Fourier transform of k³ weighted (k) EXAFS spectra of the (A) fresh Cu/mesoAl₂O₃ and (B) used Cu/mesoAl₂O₃ with the reference sample spectra of Cu, Cu₂O, CuO, and CuAl₂O₄ species

GRAPHICAL ABSTRACT

Enhanced stability of spatially confined copper nanoparticles in an ordered

mesoporous alumina for dimethyl ether synthesis from syngas

Hyungwon Ham, Jihyeon Kim, Sung June Cho, Joon-Hwan Choi, Dong Ju Moon, Jong-

Wook Bae*

The spatial confinement effect of copper nanoparticles in the ordered mesoporous Al_2O_3 showed a high stability and activity for the direct DME synthesis from syngas, by effectively suppressing the aggregation of copper crystallites and by forming an interfacial CuAl₂O₄ layer on the ordered mesoporous Al_2O_3 surfaces.

