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DIMETHYL ETHER (DME) IS PRODUCED DIRECTLY FROM CO_2 USING CATALYSTS BASED ON CU-GA/AL_2O_3

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ABSTRACT

Techniques for capturing CO_2 to create valuable chemicals and fuel can address enough of the environmental problems caused by the use of fossil fuels. The rate of methanol synthesis at the metal-oxide interface and the swift conversion of methanol to Al_2O_3 at acid sites had an impact on the production of DME.The synthesis of the intermediate is highly dependent on the texture, structure, and surface, based to an in-situ/operando Fourier Transform Infrared (FTIR) spectroscopy analysis performed under the reaction conditions (0.9 MPaG, 220-260°C).Formate species are created during the synthesis of methanol, depending on the conditions of the process. Technically speaking, the best conditions for converting CO_2 and producing DME yield are a reaction temperature of less than 260°C and a reaction pressure of 0.9 MPaG.

KEYWORDS

CO_2 hydrogenation,sol-gel method, dimethyl-ether (*DME*), *IR analysis.*

1. INTRODUCTION:

Dimethyl ether (DME) is the modest form of ether. The required properties of DME are non-toxic, colorless, non-corrosive, non-carcinogenic, and naturally friendly. DME is used as a fuel (as an alternative to petroleum-derived fuels and LNG), an intermediate in the production of many olefinic compounds (such as ethylene and propylene) and gasoline-range hydrocarbons, and as an aerosol propellant substitute for chlorofluorocarbon (CFC) materials. DME easily evaporates at ambient temperature and 0.5 MPa, as well as at 25°C and atmospheric pressure. DME is a household fuel that can be treated similarly to LPG. Coal, natural gas, biomass, and other materials are used to make DME. DME is a fuel and energy source that can be used in a variety of ways [1]. CO_2 is by far the most emitted of these gases, and thus the primary cause.However, it is also impossible to say that CO_2 emitting technology is vital to our society and that, in the short to medium term, the only way to reduce the harmful impacts of our "way of life" is to develop non-CO_2 emitting technologies for chemical production and energy generation as well as improve current methods and integrate them with CO_2 capture [2]. DME shares many of the same physical properties as LPG (liquefied petroleum gas). So compared to diesel combustion, the cetane number of DME is between 55 and 60, and the combustion processes produce lower NOx pollution[3]. DME can be stored and transferred to demand markets with minimum changes to existing infrastructure.crude oil, lignite, natural gas, residual oil, or waste materials, and biomass are all carbon-rich feedstocks that can be used to make DME.When it comes to natural gas or coal as an energy source, carbonaceous material, synthesis gas (syngas) – comprising principally H_2, CO, and CO_2 – is formed as the intermediate compound. Several

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syngas industrial methods use the synthesis and dehydration for methanol over a bifunctional catalyst.From a thermodynamic and financial standpoint, the one-step synthesis method is best suited to the two-step method. Furthermore, the single-step method may result in significant CO conversions and DME production [3,4]. The CH_3-O-CH_3 chemical formula and ratio between carbon to hydrogen (C:H). In a gaseous state, DME is invisible in a standard atmosphere (0.1 MPa at 298 K). It condenses to the liquid phase when pressed above 0.5 MPa.While liquid DME has such a density that is two-thirds that of water, gaseous DME has a density higher than that of air. The vapor pressure is like that of LPG, thus it must be handled and stored with attention. It dissolves up to 6% of its bulk in water. Due to its corrosive nature, it is incompatible with most elastomers, hence the careful selection is required to avoid seal breakdown after prolonged exposure to DME. At low mole fractions (a few percent by volume), the gas has no odor and no adverse health effects[5].

1.2. Application of DME

By weighing its benefits and drawbacks as a potential fuel to replace diesel in compression-ignition (CI) engines, it is possible to determine the significance of DME's features.

a) Oxygen contented in higher: Low production and high corrosion rates of particles would be probable under a compression-ignition (CI) engine operating in the absence of C–C, which is why it is responsible for smokeless combustion.
b) Lower boiling point: When a liquid-phase DME spray is delivered into the engine cylinder, this causes rapid evaporation.
c) Higher cetane number: From the thermochemical characteristics, the higher cetane number of DME (>55) shows the lower auto-ignition temperature and produces instantaneous vaporization. [6.7].

1.3. Limitation of DME

a) Lower enthalpy on combustion: Smaller than diesel fuel because of oxygen component particles, for DME to provide the same amount of energy as diesel, a larger injection volume and longer injection time are required.
b) Lower viscosity: Smaller than diesel fuel, resulting in the fuel supply system's leakage and minimal clearances for sealing. Because of its decreased lubricity.
c) Lower modulus of elasticity: Lesser than diesel fuel, through the differential between the two being largest at lower pressures. [8].

From CO_2, DME is produced in two different processes. It can be produced via route 1 by forming syngas by RWGSR and then converting it to DME either directly or indirectly. DME is synthesized directly from CO_2 in route 2[16].

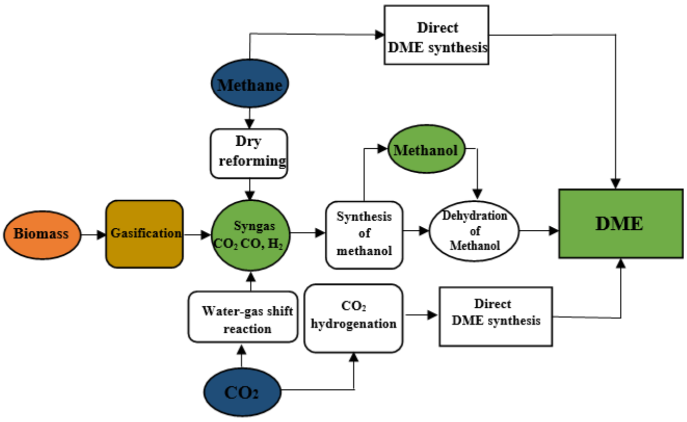


Fig. 1. Synthesis of DME using different carbon feedstocks [12].

The biggest marketplace for using DME in combination with LPG for home heating and cooking is now China;LPG is used in more than 90% of the DME produced in China. To the World LP Gas Association (WLPGA) [9] (i) DME and LPG can be used collected or disjointedly as "substitutes" for each other, and (ii) The business of LPG is prepared to accept DME use. This would not be essential to provide more than 15 to 20 volume percent of DME in LPG/DME mixes with any changes to existing distribution or customer appliances [10]. face of rising energy prices [11]. DME find some applications for diesel-powered electric power generation, particularly in congested urban areas. DME might reach NOx emissions lower than 100 ppm with proper exhaust gas recycling (EGR), as demonstrated with thermal efficiency comparable to heavy oil. NOx emissions might be decreased to around 30 ppm thermal efficiency of 40% with improved EGR [13]. China, a latecomer to DME, is the undisputed leader in DME production and application. In 2010, China overall methanol were used in the fuel market of 18 metric tons, which involved DME, MTBE, and nearly gasoline mixing. China is the world leader in DME due to clear goals use in coal products, commercial expertise, cash obtainability, and an inclination to rapidly accept novel technological concepts.Hydrogenation of CO and CO_2first formed methanol. Methanol has been thoroughly studied because it is an essential feedstock for numerous chemical processes that are widely used in the clean energy industry. These processes involve those that create products such as formaldehyde, methyl tertiary butyl ether (MTBE), acetic acid, methyl methacrylate, chloromethane, fatty acid methyl ester (FAME), and converting methanol to olefin by light olefin[14]. In addition, methanol can be utilized in fuel cell applications as a useful energy storage medium, particularly for transportation and mobile electronics. The catalytic synthesis of methanol is still fascinating for these reasons. Methanol is often made from natural gas or coal, which consists primarily of CO, H_2, and a minor amount of CO_2. As a result, hydrogenation of CO/CO_2 is a commonprocedure intended used for producing methanol by different three chemical ways [15].

[Eqs. (1) and (2)] both are CO and CO_2 hydrogenation reactions that produce methanol and occurs in an exothermic reaction. Low temperature and high pressure are most

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \Delta H^o_{298K} = -90\ \text{kJ mol}^{-1} \quad \ldots\ldots\ldots \quad (1)$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad \Delta H^o_{298K} = -49.57\ \text{kJ mol}^{-1} \quad \ldots\ldots\ldots \quad (2)$$

likely involved in these reactions. According to various reports, methanol and DME formation are best achieved at lower temperatures and higher pressures. Because of the high energy consumption, the cost of a mechanical process to generate methanol at high pressure is highly costly, and it must be put in more safety units to limit the hazards in the process of methanol feedback. [16,17,18,19].

2. EXPERIMENTAL SETUP

2.1. Preparation and procedures of hybrid catalysts

The catalysts were made using the consecutive sol-gel method with a mixture of Cu $(NO_3)_2$, Ga $(NO_3)_3$ aqueous solution. Aluminum isopropoxide (AIP), ethylene glycol (EG), nitric acid, Cu $(NO_3)_2$, and $Ga(NO_3)_3 \cdot nH_2O$ are produced from Wako pure chemical industries. The $Cu-Ga/Al_2O_3$ (24 wt% Cu; 6 wt% Ga) catalysts were prepared sol–gel method as below. In 1000 mL distilled water, mortar-crushed AIP (56.60 g) was dissolved. The mixing was stirred at ~70°C temperature.

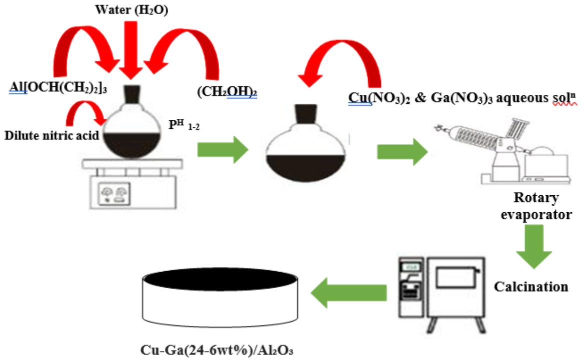


Fig. 2. Preparation procedure of Cu-Ga(24-6wt%)/Al_2O_3 catalysts by using consecutive sol-gel method.

2.2. Activity test of catalyst

The powdered catalyst was calcined at (350-800)°C and the experiments were carried out between (300-750)°C, reduced by H_2 flow for 5 hr. respectively. Approx. (14-24 mg) of catalyst loaded for the analysis of FTIR measurements. The CO_2 hydrogenation over Cu-Ga(24-6wt%)/Al_2O_3 catalyst's effectiveness and sensitivity of surface adsorption sites were examined by FTIR measurements.

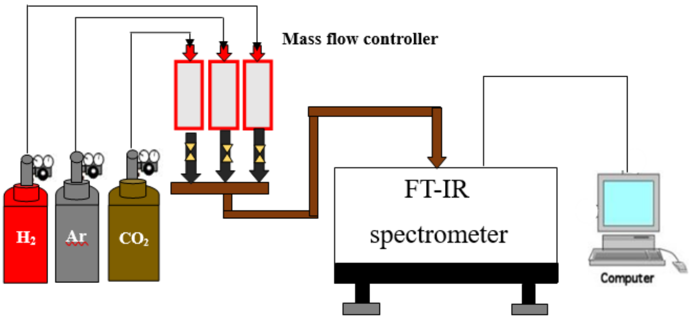


Fig. 3. Schematic diagram system.

The experiments schematically shown in Fig. 3 were performed with Cu-Ga(24-6wt%)/Al_2O_3 catalysts on JASCO FTIR 4200 with a medium-range mercury-cadmium-telluride (MCT) detector for a spectrometer equipped with, a detector cooled by liquid-nitrogen, potassium bromide (KBr) beam splitter. A ceramic holding cup with an i.d. of 5 mm and a height of 4 mm were filled with powder (14−20 mg) catalysts sample. In situ reduction of the catalyst occurred at (300-750)°C of 5 hr at H_2 (10 ml min^{-1}) during air pressure and after reduction was complete then cooled. FTIR spectroscopy in operando was obtained range between (800-3800 cm^{-1}) and an averaged scan for 15 and resolution of 2 cm^{-1}. The formation of intermediate species, methanol, and DME used to examine the mass spectrometer.

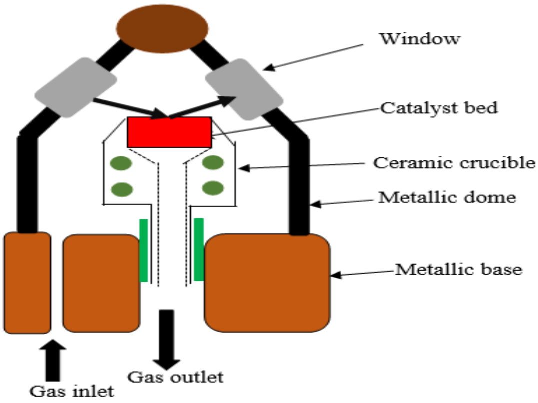


Fig. 4. Working principle of DRIFTScell.

Fig. 4 shows that events from the IR source go through the IR light sample. The catalyst sample absorbed some light and some light was reflected by the sample. Some IR lights penetrate the sample and hit the end detector. The IR radiation of the spectroscopy passes through a sample, generating some infrared vibrations by the sample and transmitting some samples.

3. Results And Discussion

3.1. DRIFTS analysis of Cu-Ga/Al_2O_3 catalysts

Operando DRIFTS spectroscopy one of the most popular procedures used to identify the different functional groups of organic compounds. FTIR is a fast and non-destructive strategy for the quantitative and qualitative analysis of different components. The peak of methoxy (CH_3O-) species shows wavenumber at 1031, 1082, and 1100 cm^{-1}. The methoxy peak was increased for adsorbing of CO_2 flow rate onto the catalyst surface.

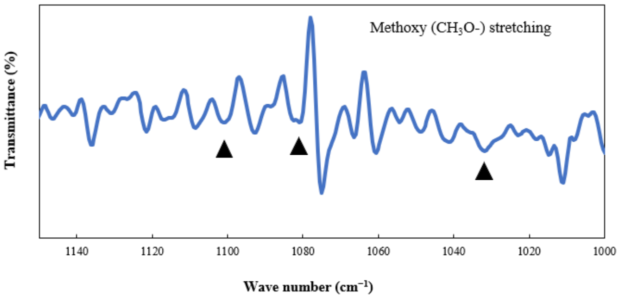


Fig. 5. DRIFT spectrum methoxy (CH_3O-) stretching over Cu-Ga(24-6wt%)/Al_2O_3 catalysts by using the sol-gel method calcined at 650°C, reduced at 600°C, and 240°C reacted temperature at 0.9 MPaG.

Figure 6, the DRIFT spectrum of methanol (C-O stretching) shows a strong adsorption band of carbon-hydrogen stretching vibration. The presence of methanol (C-O) stretching peak is assigned at 1075 cm^{-1} wavenumber. Owing to the inductive effect of carbon and hydrogen atoms, the frequency of C-H stretching corresponding to H-C=O create a weaker. The hydroxyl group is present in a broad band area of the spectrum.

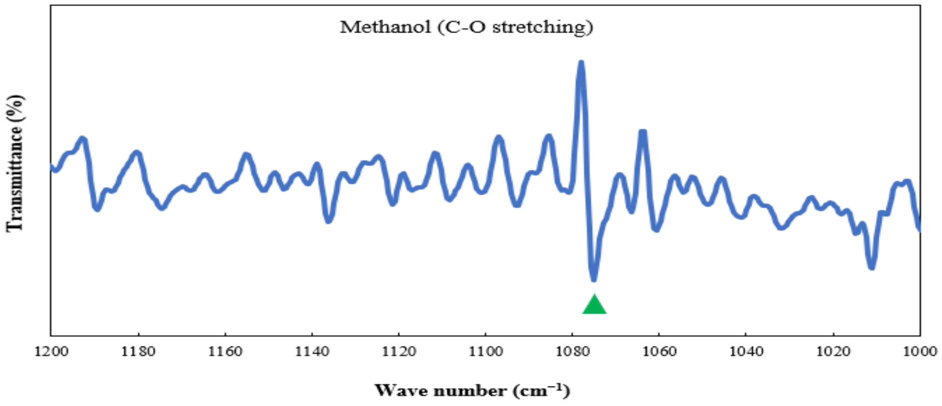


Fig. 6. DRIFT spectrum methanol (C-O) stretching over Cu-Ga(24-6wt%)/Al$_2$O$_3$ catalysts by using the sol-gel method calcined at 650°C, reduced at 600°C, and 240°C reacted temperatureat 0.9 MPaG.

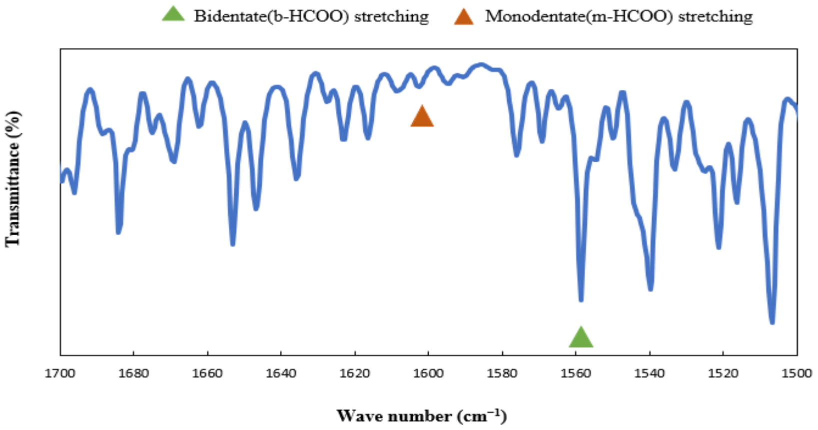


Fig. 7. DRIFT spectrum bidentate (b-HCOO) and monodentate (m-HCOO) stretching over Cu-Ga(24-6wt%)/Al$_2$O$_3$ catalysts by using the sol-gel method calcined at 650°C, reduced at 600°C and 240°C reacted temperature at 0.9 MPaG

The optimal functional group for infrared (FTIR) spectroscopy identification is the carbonyl group (C=O) because its highest vibration stretching powerful also range of wavenumber unusual. On this overview on carbonyl spectroscopy, I tried to investigate why the peak so sharp and step for use that knowledge to analyze ketones spectra. FTIR spectroscopy was successfully applied to the characterization of the functional groups. From Fig. 7, I observed a high peak at 1735 cm^{-1} indicated to the band at the carbonyl group (C=O) shifted depending on temperature from weak intense. Because of the massive difference between carbon and oxygen, carbonyl bonds are strongly polar. The high peak about 1735 cm-1 corresponds to C=O and vibrations produced whenever carboxylic acids, ketones, aldehydes, and esters were present.

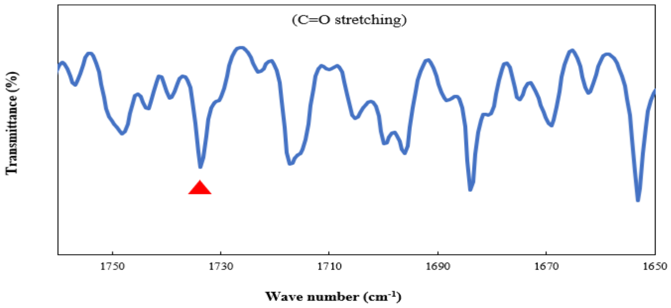


Fig. 8. DRIFT spectrum (C=O) stretching over Cu-Ga(24-6wt%)/Al_2O_3 catalysts by using the sol-gel method calcined at 650°C, reduced at 600°C, and 240°C reacted temperatureat 0.9 MPaG.

3.2. XRD analysis of Cu-Ga/Al_2O_3 catalysts

Figure. 9 shows sample XRD patterns in correlation to rising temperatures. The characterization of the diffraction peaks is shown at different temperatures. Subsequently, 350°C calcination temperature show the CuO reflection (2θ = 35.7°, 38.8°). The calcination temperature of 800°C shows the $CuAl_2O_4$ spinel peak grew larger reflection (2θ = 37.5°, 60.1°) and Ga_2O_3 form (2θ= 66.7°). When the temperature is 800°C, the spinel is larger and stronger. After that, the 500°C and 350°C calcination temperatures show the CuO peak much larger than other higher calcination temperatures getting peaks.

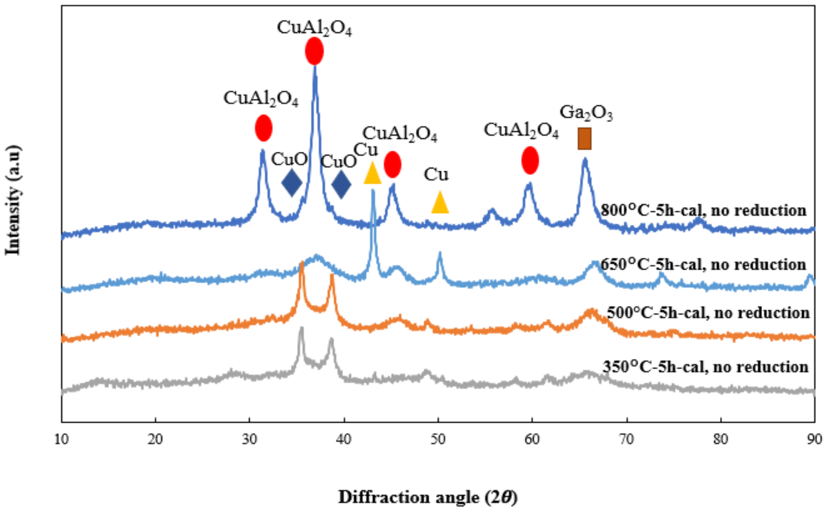


Fig. 9. XRD patterns of Cu-Ga(24-6wt%)/Al_2O_3 catalysts.

3.3. Structural characteristics of the catalysts

The metal average size, particle distribution, and Cu crystalline size were made by hybrid catalysts. It was observed that the Cu-Ga/Al_2O_3 catalysts and impact of the Cu distribution size and Cu surface layer were affected by the Cu particle size. Brunauer–Emmett–Teller (BET) technique is used for surface area. Barrett–Joyner–Halenda (BJH) method is used for pore size distribution. The N_2O titration method is used for Cu surface amount and Cu dispersion. The particle size of Cu is measured by Debye–Scherrer equation.

3.4. Direct hydrogenation of CO_2 to pro-DME: proposed reaction mechanism

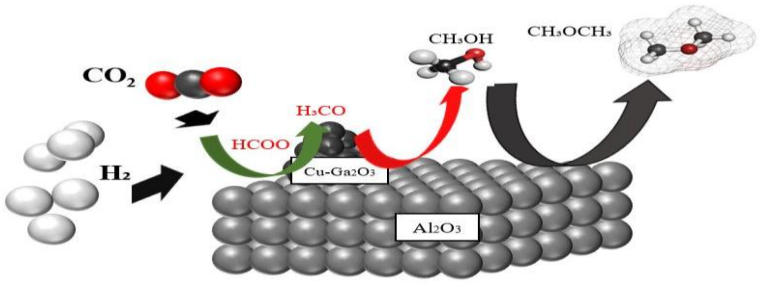
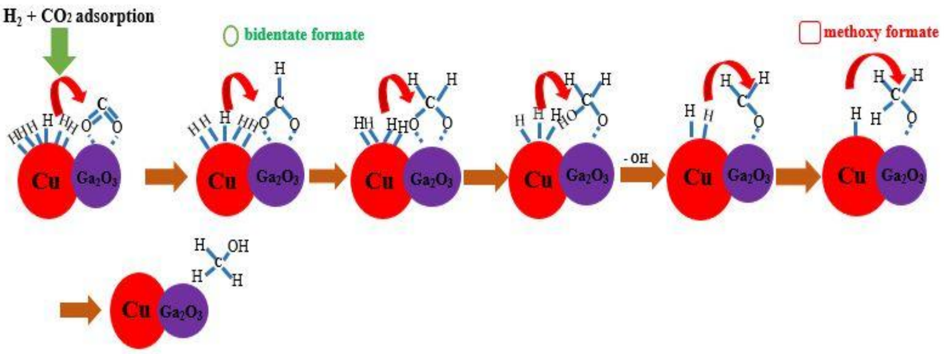


Fig. 11. The plausible process for CO_2 hydrogenation using Cu-Ga/Al_2O_3 catalysts.

Figure. 11 shows a proposed, generalized mechanism on a Cu-Ga/Al_2O_3 catalysts from CO_2-H_2 reaction to the surface reactive active sites for DME synthesis. These two distinct reactions took place when methanol and DME formed from a CO_2-H_2 mixture, occurred on the surface of Cu-Ga/Al_2O_3 catalysts. Metallic sites of Cu have been reported as H_2 activation active sites. The ensuring hydrogenation reactions methanol took place at the Cu-Ga/Al_2O_3 catalysts interfacial Cu- Ga_2O_3 sites and DME took place at the Al_2O_3 supporter. We investigated this figure the correlation between the intrinsic activity of Cu-Ga_2O_3 sites for methanol and DME production in the interfacial of Cu-Ga_2O_3 and Al_2O_3 sites quantitatively. The lattice oxygen of Cu-based catalysts are involved in the formation of HCOO species through CH_3OH synthesis from the CO_2-H_2 mixture. Normally CO_2 is adsorbed on Cu binds and nearly chemisorbed of H to the formation of H_3CO species on the surface of Cu. The CH_3OH intensities are correlated to produce H_3CO species and after that H_3CO reacts with the surface of Hto produce CH_3OH. So, the formation of surface H_3CO species a dynamically appropriate step for DME synthesis in the Cu-based catalyst.

In precise, as seen in Fig. 12, a formate intermediate (HCOO) is generated after the hydrogen atoms activate on the surface of copper. The formate pathway through conversion to formic acid (HCOOH), dioxymethylene (CH_2O_2), formic acid (HCOOH), formaldehyde (CH_2O), methoxy (CH_3O) species, and finally methanol (CH_3OH) formation. The formic acid is hydrogenated and transformed into formaldehyde (CH_2O) by separating its (OH) group.

Methanol synthesis



Methanol dehydration

Fig. 12. A proposed reaction network synthesis of DME from CO_2-H_2 reaction on Cu-Ga/Al_2O_3 catalysts.

In addition, direct CO_2 hydrogenation to DME synthesis, the initial step of the process focuses the argument on the explanation of the actual reaction mechanism. Regarding the complexity of identifying the active site of the carbon dioxide that leads to the formation of methanol intermediates and afterward dehydrated to form DME.

Producing DME by dehydrating methanol are two reactions dissociative and associative that occur over the acid sites of catalysts. Methanol has been adsorbed to one of the molecules is methanol and separately formed methoxy species on the catalyst surface. After that, reacting with other methanol molecules and DME formation (dissociative mechanism). Alternatively, the methanol molecules are co-adsorbed and associated obsessed by DME (associative mechanism). Methanol becomes adsorbed acid sites of the catalyst; methanol is adsorbed and after losing a water molecule transformed the methoxy group into a catalyst surface. Afterward, nucleophilic substitution reaction molecular methanol attacking on the catalyst surface. In this reaction production of the protonated DME and removal of water. The water molecule deprotonated the intermediates and transfer back to the proton which alumina reinforces to acid sites and leads to the DME [2,20].

CONCLUSIONS AND PROSPECTS

This work begins by developing new techniques for creating hybrid catalysts for the direct CO2 hydrogenation to DME. Improvements are made in the characterization of the important intermediates and process steps, as well as in the light of thermodynamic considerations by offering operations at high pressure and low temperature for higher CO_2 conversion and higher DME generation. The intermediates and necessary reaction pathways for CO_2 hydrogenation to DME over Cu-Ga(24-6wt%)/Al_2O_3 catalysts were investigated using the operando DRIFT technique. The catalytic hydrogenation of CO_2 occurs over Cu-based catalysts which produce methoxy, methanol, formic acid, and formate species on the catalyst Ga-oxide sites. The Cu-based catalyst is predictable to continue the catalyst formulation to active $CO_{2.}$ Hybrid systems conduct the procedure in a single step by combining the phases of metal-oxide to the methanol dehydration and DME formation. Some issues with functionality and reactivity occurs when using a single step to drive the process. The reaction mechanism of direct DME synthesis from the CO_2 hydrogenation pathway mostly focuses on the initial step.

REFERENCES

[1] Takeishi, K. and Akaike, Y., (2016)“Hydrogen production by dimethyl ether steam reforming over copper alumina catalysts prepared using the sol–gel method” Applied Catalysis A: General, 510, pp.20-26.

[2] Álvarez, A., Bansode, A., Urakawa, A., Bavykina, A.V., Wezendonk, T.A., Makkee, M., Gascon, J. and Kapteijn, F.,(2017)“Challenges in the greener production of formates/formic acid,methanol, and DME by heterogeneously catalyzed CO_2 hydrogenation processes”, Chemical reviews, 117(14), pp.9804-9838.

[3] 3.Mevawala, C., Jiang, Y. and Bhattacharyya, D., (2017)“Plant-wide modeling and analysis of the shale gas to dimethyl ether (DME) process via direct and indirect synthesis routes”, Applied Energy, 204, pp.163-180.

[4] Peral, E. and Martín, M.,(2015) “Optimal production of dimethyl ether from switchgrass-based syngas via direct synthesis. Industrial & Engineering Chemistry Research”, 54(30), pp.7465-7475.

[5] 5.Arcoumanis, C., Bae, C., Crookes, R. and Kinoshita, E., (2008) “The potential of di-methyl ether (DME) as an alternative fuel for compression-ignition engines”, A review. Fuel, 87(7), pp.1014-1030.

[6] Edgar, B.L., Dibble, R.W. and Naegeli, D.W.,(1997) “Autoignition of dimethyl ether and dimethoxy methane sprays at high pressures”, SAE transactions, pp.625-639.

[7] Francisco, J.S., (1999) “On the competition between hydrogen abstraction versus CO bond fission in initiating dimethyl ether combustion. Combustion and flame”,118(1-2), pp.312-316.

[8] Sorenson, S.C., Glensvig, M. and Abata, D.L.,(1998)“Dimethyl ether in diesel fuel injection systems”, SAE transactions, pp.438-449.

[9] Rockall, J. and de Calan, B., (2006) “DME opportunities in LP gas markets. In Second International DME Conference, London”, May, (pp. 15-17).

[10] Marchionna, M., Patrini, R., Sanfilippo, D. and Migliavacca, G., (2008) “Fundamental investigations on di-methyl ether (DME) as LPG substitute or make-up for domestic uses. Fuel Processing Technology”, 89(12), pp.1255-1261.

[11] 11.Methanex Corporation, (2011) “Annual Information Form”, March.

[12] 12.Styring, P., Dowson, G.R. and Tozer, I.O.,(2021) “Synthetic Fuels Based on Dimethyl Ether as a Future Non-Fossil Fuel for Road Transport From Sustainable Feedstocks. Frontiers in Energy Research”, 9, p.240.

[13] 13.Yoon, En Sup, Han, Chonghun., (2009) “A review of sustainable energy- recent development and future prospects of dimethyl ether. Computer Aided Chemical Engineering”, 27, 169e175.

[14] 14.Studt, F., Abild-Pedersen, F., Wu, Q., Jensen, A.D., Temel, B., Grunwaldt, J.D. and Nørskov, J.K., (2012) “CO hydrogenation to methanol on Cu–Ni catalysts: theory and experiment. Journal of catalysis”, 293, pp.51-60.

[15] 15.Pontzen, F., Liebner, W., Gronemann, V., Rothaemel, M. and Ahlers, B., (2011) “CO_2-based methanol and DME–Efficient technologies for industrial scale production”, Catalysis Today, 171(1), pp.242-250.

[16] 16. An, X., Li, J., Zuo, Y., Zhang, Q., Wang, D. and Wang, J., (2007) “A Cu/Zn/Al/Zr fibrous catalyst that is an improved CO_2 hydrogenation to methanol catalyst” Catalysis letters, 118(3), pp.264-269.

[17] 17.Pasupulety, N., Driss, H., Alhamed, Y.A., Alzahrani, A.A., Daous, M.A. and Petrov, L., (2015) “Studies on Au/Cu–Zn–Al catalyst for methanol synthesis from CO_2”, Applied Catalysis A: General, 504, pp.308-318.

[18] 18.Bozzano, G. and Manenti, F., (2016)“Efficient methanol synthesis: Perspectives, technologies and optimization strategies. Progress in Energy and Combustion Science”, 56, pp.71-105.

[19] 19.Elsernagawy, O.Y., Hoadley, A., Patel, J., Bhatelia, T., Lim, S. and Haque, N., (2020)“Thermo-economic analysis of reverse water-gas shift process with different temperatures for green methanol production as a hydrogen carrier. Journal of CO_2 Utilization”, 41, p.101280.

[20] 20. Bonura, G., Todaro, S., Frusteri, L., Majchrzak-Kucęba, I., Wawrzyńczak, D., Pászti, Z., Tálas, E., Tompos, A., Ferenc, L., Solt, H. and Cannilla, C.,(2021)“Inside the reaction mechanism of direct CO_2 conversion to DME over zeolite-based hybrid catalysts”, Applied Catalysis B: Environmental, 294, p.120255.