



# Direct synthesis of dimethyl ether from CO<sub>2</sub> hydrogenation over novel hybrid catalysts containing a Cu–ZnO–ZrO<sub>2</sub> catalyst admixed with WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts: Effects of pore size of Al<sub>2</sub>O<sub>3</sub> support and W loading content

Yossapon Suwannapichat<sup>a</sup>, Thanapa Numpilai<sup>a,b</sup>, Narong Chanlek<sup>c</sup>, Kajornsak Faungnawakij<sup>d</sup>, Metta Chareonpanich<sup>a,b</sup>, Jumras Limtrakul<sup>e</sup>, Thongthai Witoon<sup>a,b,\*</sup>

<sup>a</sup> Center of Excellence on Petrochemical and Materials Technology, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

<sup>b</sup> NANOTEC Center for Nanoscale Materials Design for Green Nanotechnology and Center for Advanced Studies in Nanotechnology for Chemical, Food and Agricultural Industries, Kasetsart University, Bangkok 10900, Thailand

<sup>c</sup> Synchrotron Light Research Institute, Nakhon Ratchasima 30000, Thailand

<sup>d</sup> Nanomaterials for Energy and Catalysis Laboratory, National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), 111 Thailand Science Park, Pathum Thani 12120, Thailand

<sup>e</sup> Department of Materials Science and Engineering, Institute of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

## ARTICLE INFO

### Keywords:

CO<sub>2</sub> hydrogenation  
Methanol  
Dimethyl ether  
WO<sub>x</sub>–Al<sub>2</sub>O<sub>3</sub>  
Hydrogen

## ABSTRACT

The present work examines the direct synthesis of dimethyl ether (DME) from CO<sub>2</sub> hydrogenation over novel hybrid catalysts containing a Cu–ZnO–ZrO<sub>2</sub> catalyst admixed with WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. The effect of pore sizes (6.6, 33 and 51 nm) of Al<sub>2</sub>O<sub>3</sub> support and W loading contents (5, 10, 15 and 20 wt%) on the physicochemical properties of WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts as well as their catalytic performance is also investigated. Characterization results from XRD, XPS and UV–vis reveal that the structure of WO<sub>x</sub> species on the surface of Al<sub>2</sub>O<sub>3</sub> is mainly related to W surface density, i.e. W loading content, which can be classified into three regions: a mixture of monotungstate species and polytungstate species at W surface density < 5.1 W nm<sup>−2</sup>, a monolayer coverage of WO<sub>x</sub> species over the surface of Al<sub>2</sub>O<sub>3</sub> at W surface density ~5.1 W nm<sup>−2</sup> and a co-existence of polytungstate species and WO<sub>3</sub> nanoparticles at W surface density > 5.1 W nm<sup>−2</sup>. The space–time yield (STY) of DME exhibits a volcanic trend as a function of W surface density with the maximum values at nearly monolayer coverage (~4.7 W nm<sup>−2</sup>) for large pores (33 and 51 nm), and above monolayer coverage (8.0 W nm<sup>−2</sup>) for small pore (6.6 nm). The hybrid catalyst with optimum Cu–ZnO–ZrO<sub>2</sub> and WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> weight ratio of 1:5 achieves the highest STY of DME of 165.6 g<sub>DME</sub> kg<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>. The long-term stability test shows a gradual decrease in activity of the hybrid catalyst which is attributed a combination of coke deposition, sintering of Cu-based catalyst and WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst and strongly adsorbed water molecules.

## 1. Introduction

Increasing energy demand and environmental issues have compelled human society to seek an alternative clean energy [1–3]. Hydrogen produced by the electrolysis of water using renewable energy such as solar and wind can be considered as an important clean energy carrier for the future [4–8]. However, the storage of hydrogen requires complex technical issues due to its high volatility and potentially explosive nature. Therefore transformation of hydrogen into small hydrogenated molecules such as methane [9], methanol [10–15],

ammonia [16] and dimethyl ether (DME) [17] is promising alternative as they can be stored and transported using existing infrastructure. Among these molecules, DME is very interesting because it can be used in a diesel engine due to its high cetane number. Since the DME molecule does not have carbon-carbon bond, the combustion of DME does not make any particulate emission so that it can be considered as a clean fuel. In addition, DME can be used as an efficient H<sub>2</sub> carrier for fuel cell application. More importantly, DME can be synthesized from recycled CO<sub>2</sub> using renewable energy which is an efficient way to achieve a sustainable carbon cycle.

\* Corresponding author at: Center of Excellence on Petrochemical and Materials Technology, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand.

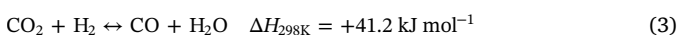
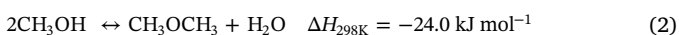
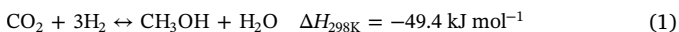
E-mail address: [fengttwi@ku.ac.th](mailto:fengttwi@ku.ac.th) (T. Witoon).

<https://doi.org/10.1016/j.enconman.2018.01.016>

Received 2 November 2017; Received in revised form 25 December 2017; Accepted 5 January 2018

0196-8904/ © 2018 Elsevier Ltd. All rights reserved.

DME can be directly synthesized from CO<sub>2</sub> and H<sub>2</sub> by a combination of methanol synthesis catalyst and an acid catalyst in a single reactor [18–21]. This approach has achieved remarkable progress over the conventional two-step process, i.e. CO<sub>2</sub> hydrogenation to methanol and its subsequent dehydration in a separate reactor, because the in-situ conversion of methanol to DME leads to a higher CO<sub>2</sub> conversion to methanol according to Le Chatelier's principle. To date, a ternary CuO–ZnO–ZrO<sub>2</sub> catalyst has been reported to be the most efficient catalyst for the synthesis of methanol from CO<sub>2</sub> hydrogenation due to its high activity and stability compared a commercial CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> [22], which is an apparent choice to be used in the single-step synthesis of DME from CO<sub>2</sub>. In contrast, a large variety of solid acid catalysts such as alumina [23,24], zeolites [25–29] and sulfated-zirconia [18] appears as candidates for the dehydration of methanol to DME. Depending on the acid strength of catalysts, methanol can be converted to various products such as DME, light olefins and other hydrocarbons, i.e. the product tends to form other hydrocarbons over catalysts with strong acid sites. For this reason, Al<sub>2</sub>O<sub>3</sub> is more suitable for the selective methanol dehydration to DME because it does not catalyze the methanol/DME to hydrocarbons due to its less strong acid sites. However, it exhibits a poorer performance in terms of activity and stability [30].



Several attempts have been made to improve the catalytic performance of Al<sub>2</sub>O<sub>3</sub> catalysts by optimizing the physicochemical properties of Al<sub>2</sub>O<sub>3</sub> [23] or modifying with various oxides such as silica, phosphorous, niobium and tungsten [31,32]. Seo et al. [23] studied the effect Al<sub>2</sub>O<sub>3</sub> phases including  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\eta$ -Al<sub>2</sub>O<sub>3</sub> on the methanol dehydration to DME. They found that  $\eta$ -Al<sub>2</sub>O<sub>3</sub> catalyst was more active than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, although total acidity and acid site density of both catalysts were nearly identical, suggesting a crucial role of Al<sub>2</sub>O<sub>3</sub> phases. The effect of SiO<sub>2</sub> addition onto the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on the methanol dehydration activity was studied by Mollavali et al. [33]. They found that higher methanol activity was mainly related to weak and medium acidic sites. Said et al. reported that the methanol dehydration over Al<sub>2</sub>O<sub>3</sub>-impregnated with 5 wt% WO<sub>3</sub> had the higher activity than the unmodified Al<sub>2</sub>O<sub>3</sub> catalyst which was attributed to the higher number and strength of acid sites [32]. Nevertheless, controversial discussions are present in the literature regarding the role of active site of WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. Macht et al. [34] reported on the alcohol dehydration activity of WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts and found that the dehydration rate followed a volcanic trend as a function of WO<sub>x</sub> surface density with a maximum value at WO<sub>x</sub> surface density of 9–10 W nm<sup>-2</sup>. This improved dehydration rate observed with increase of WO<sub>x</sub> surface density was attributed to higher strength of acid sites and the formation of Brønsted acid sites. However, Kim et al. [35] reported that the turnover rate for methanol dehydration to DME monotonically decreased as the WO<sub>x</sub> surface density increased, suggesting a greater catalytic acidity of the bare Al<sub>2</sub>O<sub>3</sub> surface compared to WO<sub>x</sub> species coordinated to the surface of Al<sub>2</sub>O<sub>3</sub>. Besides, the effect of pore size of Al<sub>2</sub>O<sub>3</sub> support on the physicochemical properties of Al<sub>2</sub>O<sub>3</sub>-supported WO<sub>3</sub> catalysts as well as their catalytic activity and stability has not yet been studied. In the present contribution, Al<sub>2</sub>O<sub>3</sub> supports with three different mean pore sizes (6.6, 33.0 and 51.0 nm) are impregnated with different tungsten contents and used in combination with a Cu–ZnO–ZrO<sub>2</sub> catalyst for direct synthesis of DME from CO<sub>2</sub> and H<sub>2</sub>. In addition, the weight ratios of the hybrid catalysts containing the Cu–ZnO–ZrO<sub>2</sub> and WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts are optimized to achieve the maximum yield of DME. The results demonstrate that the pore size of Al<sub>2</sub>O<sub>3</sub> supports determines the dispersion of tungsten and plays a vital role on the activity. Moreover, the correlation between the structure of Al<sub>2</sub>O<sub>3</sub>-supported WO<sub>3</sub> catalysts and the space-time yield of DME has been established.

## 2. Experimental

### 2.1. Preparation of CuO–ZnO–ZrO<sub>2</sub> catalyst

A CuO–ZnO–ZrO<sub>2</sub> catalyst with a Cu: Zn: Zr atomic ratio of 38.2: 28.6: 33.2 was prepared via a reverse co-precipitation method [10]. In a typical synthesis, 100 mL metal salts solution containing desired amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and ZrOCl<sub>2</sub>·8H<sub>2</sub>O was added dropwise into 500 mL of 0.1 M NaHCO<sub>3</sub> solution under stirring at room temperature. The pH of solution was adjusted to 7.5 by adding 0.1 M NaHCO<sub>3</sub>. The solution was heated from room temperature to 80 °C under continuously stirring at 400 rpm and kept constant at that temperature for 2 h. Subsequently, the precipitate was filtered and washed with deionized water (3 L). The resulting product was dried at 100 °C for 24 h and then calcined in air at 350 °C for 2 h. The physicochemical properties of the CuO–ZnO–ZrO<sub>2</sub> catalyst are reported in our previous work [10].

### 2.2. Preparation of WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts

The alumina supports with different mean pore size (Sigma Aldrich) were impregnated with the desired amount of ammonium (para) tungstate hydrate (H<sub>4</sub>N<sub>10</sub>O<sub>42</sub>W<sub>12</sub>·xH<sub>2</sub>O, Sigma Aldrich) to achieve the tungsten loading contents of 5, 10, 15, 20 and 25 wt%. The slurry mixture was stirred at 60 °C for 5 h, dried at 100 °C overnight and then calcined at 800 °C for 4 h. The resulting catalysts are designated as X-AS, X-AM and X-AL, where X was tungsten loading content by weight percent and S, M and L were referred to the mean pore size of alumina supports with small, medium and large pores, respectively.

### 2.3. Catalyst characterization

N<sub>2</sub>-sorption isotherms, pore size distribution, BET surface area and total pore volume of all catalysts were measured with a Quantachrome Autosorb-1C instrument at –196 °C. Prior to measurement, the samples were degassed at 200 °C for 24 h. Pore size distribution was calculated from the desorption branch of the isotherms using the Barrett–Joyner–Hallenda (BJH) method. The BET surface area (S<sub>BET</sub>) was estimated for relative pressure values (P/P<sub>0</sub>) ranging from 0.05 to 0.30 and the total pore volume was calculated at P/P<sub>0</sub> of 0.995.

X-ray diffraction (XRD) patterns of all WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were recorded with a Bruker D8 Advance diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154060$  nm). The measurements were obtained in a range of 5–75° in the scan mode of 0.02° step size at room temperature.

Absorption spectra and band gap energy of different WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were collected with a UV–visible diffuse reflectance spectroscopy (JASCO: V-670) at room temperature using BaSO<sub>4</sub> as a reference standard. The obtained reflectance spectra were transformed to the plot of (ah $\nu$ )<sup>1/2</sup> versus photon energy (h $\nu$ ). The point of intersection of the tangent line through the slope with its lower curve baseline was estimated the band gap energy (E<sub>g</sub>).

X-ray photoelectron spectroscopy (XPS) of different WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts was carried out at beamline 5.3 of the Synchrotron Light Research Institute (SLIRI), Thailand with a PHI5000 Versa Probe II (ULVAC-PHI, Japan) using Mg K $\alpha$  radiation source. C1s peak at 284.8 eV was used as reference to calibrate all binding energies and the XPS data were processed and analyzed with PHI MultiPak XPS software.

Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was performed to measure the total acidity of catalysts. In a typical experiment, a WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst (100 mg) was placed in the reactor, heated under He flow at 550 °C for 2 h and subsequently cooled down to 100 °C. Once the 100 °C temperature was reached and stabilized, 10% v/v NH<sub>3</sub> in He was introduced into the system for 1 h. After that, the feed was then switched to pure He for 1 h to remove the physisorbed NH<sub>3</sub>. The NH<sub>3</sub> desorption measurement was conducted in a flow of He (50 mL min<sup>-1</sup>) at a heating rate of 15 °C min<sup>-1</sup> from 100 °C to 500 °C.

Download English Version:

<https://daneshyari.com/en/article/7159120>

Download Persian Version:

<https://daneshyari.com/article/7159120>

[Daneshyari.com](https://daneshyari.com)