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Direct synthesis of dimethyl ether from CO ₂ hydrogenation over Cu–ZnO–
ZrO ₂ /SO ₄ ²⁻ –ZrO ₂ hybrid catalysts: Effects of sulfur to zirconia ratios
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1 Abstract

2	Sulfated zirconia catalysts were prepared by a direct sulfation method and were
3	admixed with CuO-ZnO-ZrO ₂ catalyst for the direct synthesis of DME from CO_2
4	hydrogenation. The effects of sulfur to zirconia ratios on the physicochemical properties,
5	activity, selectivity and stability of the catalysts were investigated. The sulfur loading
6	content significantly influenced on the structure and surface chemistry of the catalysts. The
7	addition of small amount of sulfur (5-15 wt%) created numerous mesopores on the catalyst
8	surface, remarkably enhancing the surface area and total pore volume. However, at high
9	sulfur loading (20-30 wt%), the mesopores tended to merge and form a larger pore. The
10	detailed characterization by FT-IR, XANES and NH ₃ -TPD reveals that the sulfated
11	zirconia with low sulfur content (5-10 wt%) mainly contained weak acid sites and acted as
12	Lewis acids. Increasing sulfur loading (15-30 wt%) resulted in the formation of Brønsted
13	acid sites, increasing the acid strengths. The sulfated zirconia catalyst at 20 wt% sulfur
14	loading achieved a superior DME productivity of 236 g_{DME}/kg_{cat} h at a reaction temperature
15	and pressure of 260 °C and 20 MPa. However, after 75 h of a time-on-stream experiment,
16	the sulfated zirconia catalyst lost approximately 16.9% of its initial activity while a
17	commercial H-ZSM-5 catalyst was more stable as only 2.85% reduction was observed.
18	
19	Keywords: Carbon dioxide: Sulfated zirconia catalysts: Dimethyl ether: Heterogeneous

19 Keywords: Carbon dioxide; Sulfated zirconia catalysts; Dimethyl ether; Heterogeneou20 catalysis.

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1 1. Introduction

2 Exploring novel alternative fuels is necessary in order to meet the high global 3 demand for energy and power and reduce greenhouse gases, especially carbon dioxide 4 (CO₂), released into the atmosphere. The combustion of fossil fuels is the main human 5 activity that causes a drastic increase in the concentration of CO_2 in the atmosphere, which is believed to be the major reason for rapid climate change [1]. For these reasons, the 6 7 production of alternative fuels created from CO₂ is attractive as a prospective solution both 8 for high energy demand and for global warming concerns [2–4]. Among the alternative 9 fuels, dimethyl ether (DME) is considered a promising economical transportation fuel 10 because it can be used as an efficient H₂ carrier for fuel cell applications, a fuel source in diesel engines, and a replacement for cooking gas (Liquified Petroleum Gas; LPG) [5-7]. 11 12 In addition, DME is a clean fuel because the combustion of DME with an excess of oxygen 13 produces no particulate matter and low NO_x emissions.

14 DME can be produced from CO_2 in a single step by mixing a catalyst for methanol 15 dehydration with a catalyst for methanol synthesis in a close proximity. This process has 16 received increased attention from researchers because in situ conversion of methanol to 17 DME would become a driving force to overcome the limitation of thermodynamic 18 equilibrium for CO_2 hydrogenation to methanol [8]. In order to obtain a high yield of 19 DME, an excellent catalyst that can effectively convert CO_2 to methanol is required. Many 20 kinds of bimetallic compounds, e.g., Cu-Zn [9], Pd-Ga [10], Ni-Ga [11] supported on metal 21 oxides have been investigated for methanol synthesis from CO₂ hydrogenation. Among 22 them, Cu-Zn bimetallic compound has been found to be the most efficient catalyst in terms 23 of performance and cost, and therefore they are considered as the methanol conversion 24 catalyst in this study. To date, several works have focused on the modification of Cu-based 25 catalysts in order to enhance the catalytic activity and stability. Arena et al. [12] showed 26 that ZrO₂ modified Cu-Zn oxide-based catalysts were more active for the methanol

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synthesis from CO₂ hydrogenation than conventional Cu-ZnO-Al₂O₃ catalysts. Wengui et
al. [13] modified the conventional Cu-ZnO-Al₂O₃ catalyst by adding a small amount of La
and found that La could enhance the dispersion of Cu and reduce the CuO crystallite size.
Zhang et al. [14] reported that by adding 0.5 wt% V₂O₅ onto Cu-ZnO-ZrO₂ catalyst CO₂
conversion and DME selectivity increased 12.5% and 6.7% compared to the unmodified
Cu-ZnO-ZrO₂ catalyst. However, very few studies have considered on the improvement of
acid catalysts [15].

8 Several solid acid catalysts such as alumina (Al₂O₃), modified alumina, and H-9 ZSM-5 were extensively studied in the dehydration of methanol. The alumina catalysts 10 exhibited a good performance in terms of both methanol conversion and DME selectivity. 11 However, the alumina catalysts rapidly deactivated due to a strong adsorption of water 12 molecules on Lewis acid sites [16]. H-ZSM-5 had a strong resistance towards water 13 adsorption [17]. Nevertheless, H-ZSM-5 usually contained a narrow pore size, which 14 limited the diffusion of reactant molecules from the surface to the active sites located in the 15 pores. This indicated that only the active sites on the external surface of the H-ZSM-5 16 could be used effectively. Moreover, the strong acid sites on the surface of HZSM-5 could 17 lead to coke and hydrocarbon formation as secondary products [17, 18]. The modified 18 Al_2O_3 catalyst with 1 wt.% titania was reported to increase the dehydration rate and to 19 minimize the coke formation. However, the optimum operating temperature over this 20 catalyst was ca. 400 °C, which was considerably higher than the optimum temperature 21 (220–280 °C) for CO₂ hydrogenation to methanol [12, 19, 20]. Thus, the development of 22 the acidic catalysts for this process is still desired.

Interestingly, sulfated zirconia catalysts have been reported to be super acid catalysts because their catalytic activity is relatively high in alkane isomerization [21–24], esterification [21, 25–29] and alcohol dehydration [21, 30–33]. With the tunable acid-base properties over sulfur loading content, sulfated zirconia materials could act as bifunctional

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1 catalysts for the isomerization of glucose to fructose and the dehydration of fructose to 5-2 HMF [34]. Despite the significant number of papers reporting the high activity of sulfated 3 zirconia catalysts, a few studies have considered the use of sulfated zirconia as catalysts for 4 methanol dehydration to DME production [30–32], and the performance of a Cu/ZnO/ZrO₂ 5 catalyst mixed with various sulfated zirconia catalysts for the direct synthesis of DME from CO_2 hydrogenation has not yet been reported. In this work, the sulfated zirconia catalysts 6 7 with different sulfur contents were therefore prepared by a direct sulfation method and used 8 in a combination with a $Cu/ZnO/ZrO_2$ catalyst for the direct synthesis of DME from CO_2 9 hydrogenation. The catalytic performance in terms of activity and stability of the sulfated 10 zirconia catalysts is discussed on the basis of their structure and surface acidity. Moreover, 11 a reaction mechanism for methanol dehydration to DME over the sulfated zirconia catalysts 12 is proposed based on evidence of various characterization techniques.

13

14 **2. Experimental**

15 2.1. Catalyst preparation

A CuO-ZnO-ZrO₂ catalyst at a Cu:Zn:Zr atomic ratio of ~4:2:4 was prepared by 16 17 reverse co-precipitation method. Note that the effect of metal oxide compositions on the 18 activity and selectivity of methanol production from CO_2 hydrogenation has been primarily 19 investigated and we found that Cu:Zn:Zr with the molar ratio of $\sim 4:2:4$ could provide an 20 excellent catalytic performance in terms of yield of methanol and stability. As a result, this 21 particular composition was applied in the present study. A metal salts solution (ca. 100 22 mL) of Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O and ZrOCl₂·8H₂O (Sigma Aldrich) was slowly 23 added into a 0.1 M NaHCO₃ solution (500 mL) under stirring at room temperature. The pH 24 of the solution was adjusted to 7.5 by adding 0.1 M NaHCO₃ solution. The mixture was 25 continuously stirred at 400 rpm for 2 h. The precipitate was filtered and washed with 3,000 26 mL deionized water. Subsequently, the obtained product was dried at 100 °C for 24 h and

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1 calcined at 350 °C for 2 h. The textural properties of the prepared catalyst are listed in

2 Table 1.

6

3 **Table 1** Chemical compositions and textural properties of the CuO-ZnO-ZrO₂ catalyst.

4	Catalyst	Chemical composition (mol %) ^a			BET surface	Average pore	Total pore volume
		CuO	ZnO	ZrO ₂	(m^2/g)	(nm)	(cm ² /g)
	CuO-ZnO-ZrO ₂	37.47	21.53	41.00	142	26.4	0.94

5 ^a The chemical compositions of the catalyst were determined by ICP technique.

A series of sulfated zirconia catalysts with different sulfur loadings were accomplished according to the procedure described by Sun et al. [35]. In a typical preparation process, $ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_2SO_2$ were ground in an agate mortar for 20 min at room temperature. After standing for 18 h at room temperature in air, the sample was calcined at 550 °C for 5 h. The hybrid catalysts were prepared by a physical mixing by a mortar of methanol synthesis catalyst and acid catalyst with a mass ratio of 1:2.

13 A commercial zeolite catalyst (Na⁺ZSM-5 with Si/Al ratio of 24, SH-55 from 14 ALSI-PENTA Zeolithe GmbH (APZ)) was transformed to H-ZSM-5 via an ion-exchange 15 method using ammonium nitrate (NH₄NO₃) solution. Typically, 1.5 g catalyst was placed 16 into a bottle. 100 ml of 0.1 M NH₄NO₃ solution was added. The exchange process was 17 performed at 80°C for 2 h under vigorous stirring. After that, the exchanged sample was 18 washed with 100 mL of deionized water to remove the excess NH_4^+ ions. The process was 19 repeated for 3 times. Then, the obtained NH_4^+ZSM -5 sample was dried overnight at 110°C. 20 Finally, the resulting sample was calcined in air at 550°C for 6 h in order to obtain the H-21 ZSM-5 catalyst.

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The BET surface area, pore size distribution and pore volume of all catalysts were determined by N₂-sorption measurement with a Quantachrome Autosorb-1C instrument at -196 °C. Prior to measurements, the samples were degassed at 200 °C for 24 h. Pore size distributions of the samples were determined from the adsorption branch of the isotherms in accordance with the Barrett-Joyner-Hallenda (BJH) method. The specific BET (S_{BET}) was estimated for P/P₀ values to be between 0.05–0.30. The total pore volume was measured at a relative pressure (P/P₀) of 0.995.

8 The surface morphology and surface chemical compositions of the sulfated zirconia 9 catalysts were assessed with the application of a scanning electron microscope (SEM; FEI 10 Quanta 450) equipped with energy-dispersive X-ray spectroscopy (EDS). The SEM 11 measurement was taken at 20.0 kV. The samples were sputter–coated with gold prior to 12 analysis.

13 X-ray diffraction (XRD) patterns of all catalysts were attained on a diffractometer 14 (Bruker D8 Advance) with Cu-K α radiation. The measurements were made at temperatures 15 in a range of 15–70° on 2 θ with a step size of 0.05°. The diffraction patterns were analyzed 16 according to the Joint Committee on Powder Diffraction Standards (JCPDS).

The sulfate content in each sample was determined with a DSC-TGA 2960 thermal analyzer (TA Instruments). A 50 mg sample was loaded into an alumina sample pan. In order to remove pre-adsorbed H₂O, the sample was heated from room temperature in a flow of pure N₂ (100 mL/min) at a rate of 10 °C/min until 400 °C was achieved, then it was kept at that temperature for 30 min. Subsequently, the temperature was linearly raised to 1100 °C at a rate of 10 °C/min. The sulfate content was calculated from the difference in weight between the sample at 400 °C and 1,100 °C.

FT-IR spectra of the sulfated zirconia catalysts were obtained with a spectrophotometer (Bruker Tensor 27) in the range of $400-4000 \text{ cm}^{-1}$ with a resolution of 4 cm⁻¹. The sample preparation included the amalgamation of a fine powder of each
 sample with KBr powder.

3 Sulfur K-edge X-ray Absorption Near Edge Structure (XANES) of fresh catalysts 4 was recorded at room temperature in the fluorescent mode using a silicon (111) doublecrystal monochromator at beamline 5, Synchrotron Light Research Institute (SLRI), 5 6 Nakhon Ratchasima, Thailand. The collected energy range was from 2372 to 2592 eV, with 7 0.2 eV steps from 2442 to 2552 and 10 eV steps outside that range. A pure $(NH_4)_2SO_4$ was 8 also measured as a standard reference material. The pre-edge and post-edge background 9 subtraction followed by a normalization procedure of all XANES spectra was achieved 10 using the ATHENA program.

11 Acidity measurements were performed by thermogravimetric technique using 12 ammonia as a probe molecule. A 20 mg sample was pretreated in a flow of He (50 mL/min) at a rate of 10 °C/min until 550 °C was achieved; the 550 °C temperature was 13 14 maintained for 30 min, then the sample was cooled to 100 °C. Once the 100 °C 15 temperature was reached and stabilized, 10% v/v NH₃ (He as a balance gas) with a flow 16 rate of 50 mL/min was introduced into the system for 1 h. Subsequently, the $10\% \text{ v/v NH}_3$ 17 flow was disconnected and a He flow was introduced for 1 h to remove physisorbed NH₃. 18 The NH₃ desorption measurement was conducted in a flow of He (50 mL/min) at a heating 19 rate of 5 °C/min from 100 °C to 600 °C. The amount of acidity was determined from the 20 weight loss due to the desorption of NH₃.

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22 2.3. Catalytic activity test

CO₂ hydrogenation to DME was carried out in a fixed-bed stainless steel reactor (7.75 mm inner diameter). 0.15 g hybrid catalyst was diluted with 1.35 g inert silica sand (75–150 μ m). The catalyst was reduced *in situ* under atmospheric pressure with flowing H₂ (60 mL/min) at 300 °C and a heating rate of 2 °C/min for 4 h. After the reduction, the Published on 28 January 2015. Downloaded by Selcuk University on 02/02/2015 06:59:07.

temperature was cooled to 180 °C under flowing N₂; subsequently a flow of CO₂ and H₂ 1 2 mixture (CO_2 :H₂ molar ratio of 1:3) was fed through the reactor. The feed flow rate was set 3 at 60 mL/min. The reactor pressure was slowly raised to 20 bars, and the reactor was heated to a variety of temperatures (240, 260, 270, 280 and 300 °C). The effluent gaseous 4 products were analyzed by using gas chromatography. Analysis of H₂, CO, CO₂, and N₂ 5 6 was performed using GC-2014 gas chromatography equipped with a thermal conductivity 7 detector (TCD) and a Unibead-C column. Methanol, DME and other hydrocarbon products 8 were analyzed by using GC 8A equipped with a flame ionization detector (FID) and a 9 Chromosorb WAW (20% PEG) column. The activity-selectivity data were calculated by 10 mass balance from an average of three independent measurements. The errors were within \pm 2%. CO₂ conversion to oxygenated compounds, yield of DME and yield of CO are 11 12 defined as follows:

13 CO₂ conversion to oxygenated compounds (%) =

$$\frac{(\text{moles methanol} + (2 \text{ x moles DME})) \times 100}{\text{moles CO}_{2 \text{ in}}}$$
(1)

15 Yield of DME (%) =
$$\frac{2 \text{ x moles DME} \times 100}{\text{moles CO}_{2.in}}$$
 (2)

16 Yield of CO (%) =
$$\frac{\text{moles CO} \times 100}{\text{moles CO}_{2.in}}$$
 (3)

17

18 The stability of the catalysts is presented in terms of space-time yield of methanol 19 and DME (grams methanol or DME grams catalyst⁻¹ time⁻¹) as a function of time-on-stream 20 defined as follows:

21 Space-time yield of methanol =

$$\frac{\text{moles methanol}}{\text{moles CO}_{2,\text{in}} \text{ x total amount of catalyst x MV}} \times V_{\text{CO}_2} \times \text{MW}_{\text{methanol}}$$
(4)

=

23 Space-time yield of DME

where V_{CO2} is the volumetric flow of CO_2 (cm³ min⁻¹), MW_{methanol} and MW_{DME} are the molecular weight of methanol and DME (grams mol⁻¹), and MV is the molar volume of ideal gas, 22,400 cm³ mol⁻¹. Eq. 1-3 and Eq. 4-5 are used in Fig. 6 and Fig. 8, respectively.

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6 **3. Results and discussion**

7 3.1 Catalyst characterization

Figure 1 shows the N₂ adsorption-desorption isotherm (Fig. 1a) and the 8 9 corresponding pore size distribution (Fig. 1b) of the sulfated zirconia catalysts prepared at 10 different sulfur loading contents. The isotherm of pure ZrO_2 was a typical type IV with a 11 H4 hysteresis loop, a characteristic mesopore structure formed by the aggregates of the 12 plate-like particles giving rise to slit-shaped pores. The pore size distribution of ZrO₂ was 13 broad, ranging from 4 to 30 nm. When 5-15 wt% sulfur was loaded onto the ZrO_2 , the type 14 IV isotherm was observed, but the hysteresis loop was changed to H2, indicating that the 15 ink-bottle-like structure caused by the compacts of the non-uniform size spherical particles 16 was present. In comparison to the ZrO_2 product, the mesopores ranging from 2 to 10 nm of 17 the 5S-ZrO₂, 10S-ZrO₂ and 15S-ZrO₂ products becomes more pronounced. When the sulfur 18 content was increased to 20 wt% (20S-ZrO₂), type IV-II composite isotherms were 19 observed, indicating the presence of both mesopores and macropores. At the highest sulfur 20 content, 30 wt% (30S-ZrO₂), mesopores (2–20 nm) were no longer observed, and instead 21 only macropores are obtained.

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Figure 1 N₂ adsorption-desorption isotherm (a) and pore size distribution (b) of sulfated zirconia catalysts calcined at 550 °C.

5 Table 2 lists the results regarding the BET surface area, pore volume, and average 6 pore diameter of the sulfated zirconia catalysts. The BET surface area and the pore volume of pure ZrO_2 were found to be 26 m²/g and 0.08 cm³/g, respectively. At 5–15 wt% of the 7 8 sulfur addition, the BET surface area and pore volume increased remarkably compared to 9 those of pure ZrO₂. The 10S-ZrO₂ exhibited the highest BET surface area and the largest pore volume, 89 m²/g and 0.18 cm³/g, respectively. The BET surface area decreased 10 significantly, to 36 m²/g to 7 m²/g, when sulfur content increased to 20 and 30 wt%, 11 12 respectively. This discrepancy in BET surface area can be explained as follows: at 5-15 13 wt% of the sulfur content, the ammonium sulfate is highly dispersed onto the ZrO₂ surface, 14 creating the numerous mesopores observed after the calcination. However, at high sulfate 15 content (20–30 wt%), the sulfate species might fully cover the ZrO_2 surface, resulting in 16 the reduction of BET surface areas and the generation of the larger pores.

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	Catalysts	BET	Pore	Sulfur content	Weak	Medium	Total acid
		surface area	volume	(wt%)	acid sites	acid sites	sites
		(m^2/g)	(cm^3/g)		(µmol/g)	(µmol/g)	(µmol/g)
-	ZrO ₂	26.1	0.08	Not detectable	24	-	24
	5S-ZrO ₂	66.7	0.13	$1.00^{\rm a}, 0.92^{\rm b}$	75	20	95
	$10S-ZrO_2$	89.2	0.18	$1.20^{a}, 1.56^{b}$	87	42	129
	$15S-ZrO_2$	74.9	0.17	3.20 ^a ,4.24 ^b	54	160	214
	$20S-ZrO_2$	36.0	0.13	7.00 ^a ,12.42 ^b	45	261	306
	30S-ZrO ₂	6.6	0.06	$14.00^{\rm a}, 17.78^{\rm b}$	29	140	169

1 **Table 2** Textural, sulfur content and surface acidic properties of the catalysts

3 ^a The sulfur content determined by the TGA analysis.

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4 ^b The sulfur content measured by the SEM-EDS analysis.

6 The thermal stability and the sulfate content of the sulfated zirconia catalysts, 7 shown in Fig. 2, were analyzed by TG and DTG under nitrogen flow condition. Every sample showed weight loss at temperatures below 100 °C, a result ascribed to the 8 9 desorption of physically adsorbed water molecules. The samples prepared with low sulfur 10 contents (5S-ZrO₂ and 10S-ZrO₂) exhibited a small weight loss beginning at about 750 °C and ending at 900 °C, possibly due to the evolution of SO₃ decomposed from the sulfate ion 11 12 bonded to the zirconia surfaces. With further increase in the sulfur content $(15S-ZrO_2,$ 20S-ZrO₂ and 30S-ZrO₂), the DTG curve exhibited an additional peak around 726 °C. This 13 14 implies that the sulfate that forms on the surface of the zirconia at high coverage is less 15 stable than that at low coverage. In other words, the number of the coordinated 16 configuration between sulfate and zirconia of the catalysts with high sulfate coverage is 17 lower than the catalysts with low sulfate coverage.



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2 Figure 2 TG (a) and DTG (b) curves of the sulfated zirconia catalysts calcined at 550 °C.

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4 TG tests determined the catalysts' sulfur content on the basis of the difference in 5 weights at 200 and 1100 °C. The results are shown in Table 2 together with the sulfur content measured by SEM-EDS. The TG and SEM-EDS measurement agree for catalysts 6 7 prepared with low sulfur contents (5S-ZrO₂ and 10S-ZrO₂). However, for catalysts 8 prepared at higher sulfur contents (15S-ZrO₂, 20S-ZrO₂ and 30S-ZrO₂), the SEM-EDS 9 measurements were appreciably higher than the TG measurements. This suggests that, at 10 high sulfur content, sulfate species almost completely cover on the surface of the zirconia, 11 preventing the SEM-EDS analysis from detecting the ZrO₂. Note that the catalysts' sulfur 12 contents were obviously different from those of the starting composition, which could be 13 due to the fact that the catalysts were pre-calcined at 550 °C prior to the TG and SEM-EDS

3 The FT-IR spectra of the sulfated zirconia catalysts prepared at different sulfur contents are shown in Fig. 3. The pure ZrO_2 showed bands between 700 and 418 cm⁻¹, 4 characteristics of crystalline zirconia. The 5S-ZrO₂ and 10S-ZrO₂ exhibited bands at 995, 5 1053, 1136 and 1196 cm⁻¹, characteristic peaks for the S-O stretching vibration modes of 6 the coordinated SO_4^{2-} species on the zirconia surface. The band at 1400 cm⁻¹ was assigned 7 to the stretching vibrations of S=O bond in the sulfate groups. The band at 1612 cm^{-1} was 8 attributed to δ_{O-H} bending frequency of water molecules associated with the sulfate groups. 9 10 As the sulfur loading was increased up to 15 wt% (15S-ZrO₂), the distinct peaks between 990-1200 cm⁻¹ were no longer observed, and one broad peak appeared instead. With 11 further increase of the sulfur content from 15 to 30 wt% (20S-ZrO₂ and 30S-ZrO₂), this 12 13 peak, which indicates a complex poly-sulfate surface species [36], became more dominant. 14 It was interesting to see that the spectral splitting between the ν (S=O) and ν (S=O) of the 5S-ZrO₂ and 10S-ZrO₂ (200 cm⁻¹) catalysts was much larger than that between the 15S-15 ZrO₂, 20S-ZrO₂ and 30S-ZrO₂ catalysts, indicating that tridentate sulfate ions coordinated 16 17 to the zirconia at the low sulfur contents while a 2-fold coordinated configuration was 18 formed at high sulfur contents. This FT-IR interpretation was clearly consistent with the 19 TG analysis (Fig. 2), i.e. the catalysts with low sulfur contents had a higher coordination 20 configuration. This finding was also supported by the theoretical study by Haase and Sauer [37]. The band at 1340 cm⁻¹, assigned to the bending vibration of Zr–OH groups [32, 38], 21 22 was observed only for the catalysts with high sulfur contents (15S-ZrO₂, 20S-ZrO₂ and 23 30S-ZrO₂).

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Figure 3 FTIR spectra of the sulfated zirconia catalysts calcined at 550 °C.

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4 Sulfur K-edge X-ray absorption near edge structure (XANES) spectra was used to 5 investigate the sulfate species. The first derivative analyses on the spectra were performed 6 in order to detect absorption edges of overlapping species. The sulfur K-edge XANES 7 spectra and first derivative spectra of $(NH_4)_2SO_4$ and sulfated zirconia samples are shown 8 in Figure 4. The $(NH_4)_2SO_4$ showed a white line around 2483.2 eV. The sulfur K-edge 9 XANES spectra of all sulfated zirconia catalysts were similar to the (NH₄)₂SO₄ sample, 10 indicating that the sulfur species form as a sulfate group. However, the shape of the white 11 line of the sulfated zirconia catalysts was slightly different than that of the (NH₄)₂SO₄ 12 sample. In addition to the white line at 2483.2 eV, an absorption peak at 2475.6 eV was 13 present for the sulfated zirconia catalysts with high sulfur contents (15S-ZrO₂, 20S-ZrO₂ 14 and 30S-ZrO₂). This suggests that a portion of the sulfate group was reduced to lower 15 valence states [39]. The first derivative on these spectra showed a more distinctive

difference in the white lines of the $(NH_4)_2SO_4$ and the catalysts (Fig. 4b). The firstderivative of the sulfated-zirconia catalysts had two peaks: one at 2480.2 eV and another at 2483.2 eV. The latter peak was in the same position as that of $(NH_4)_2SO_4$ and the former peak was interpreted as indicating a protonated sulfate [40–42]. It can be seen that the former peak was much more developed when the sulfur content was increased and that it correlated to the appearance of the FT-IR band at 1340 cm⁻¹ (Fig. 3), indicating that the protonated sulfate occurred at high sulfate surface coverage.



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Figure 4 Raw data (a) and first derivative of sulfur K-edge XANES spectra (NH₄)₂SO₄ and
 sulfated-zirconia materials.

The strength and overall concentration of the acid sites of the sulfated zirconia catalysts were determined by NH₃-TPD; the results are shown in Fig. 5. The pure ZrO_2 catalyst showed one broad low-temperature desorption peak ranging from 100 to 200 ^{0}C , indicating the presence of weak acid sites. The sulfation treatment at low sulfur content (5S-ZrO₂) increased the number of the weak acid sites and also generated medium acid sites, corresponding to the desorption of NH₃, in the range of 240–400 ^{0}C , with the maximum at 266 ^{0}C . As the sulfur content was increased to 10 wt% (10S-ZrO₂), the

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second peak appeared to be broader and of somewhat higher intensity than it did for the 5S-ZrO₂ catalyst. With an even higher sulfur content (15S-ZrO₂, 20S-ZrO₂ and 30SZrO₂), the second peak shifted towards to a higher desorption temperature, indicating an increase in the acid strengths corresponding to the presence of the protonated sulfate species as observed by sulfur K-edge XANES analyses (Fig. 4).



6

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Figure 5 NH₃-TPD profiles of the sulfated zirconia catalysts calcined at 550 °C.

8

9 The number of acid sites of all samples is shown in Table 2. The pure ZrO_2 had a 10 low number of total acid sites (24 µmol/g). The addition of sulfur markedly enhanced the 11 total number of acid sites. The doping 5–20 wt% sulfur provided the total acid contents 12 higher than the pure ZrO_2 at 3.96–12.75 times. Further increase in sulfur content to 30 wt% 13 caused a significant decrease in the number of the total acid sites, suggesting some sulfate 14 groups had become embedded in the bulk of the sulfated zirconia catalysts.

15

16 3.2 Catalytic activity results

17 CO₂ hydrogenation was tested over CuO-ZnO-ZrO₂/sulfated-zirconia catalysts in a
 18 fixed-bed reactor at 20 bars. The catalytic activities were determined after 3 h on stream at

the same GSHV. For all catalysts, CO, methanol and DME were found to be the major products; each also produced a trace amount of methane. The catalytic performance of the sulfated-zirconia catalysts prepared at different ratios is shown in Fig. 6 in terms of CO₂ conversion to oxygenated compounds (Fig. 6a), yield of DME (Fig. 6b) and yield of CO (Fig. 6c). The oxygenated compounds included methanol and DME produced from CO₂ hydrogenation and methanol dehydration, respectively.

Over the sulfur-free catalyst (ZrO₂), and at a reaction temperature of 240 °C, the
CO₂-to-oxygenated compounds conversion rate (Fig. 6a) was 2.6%. The CO₂ conversion
decreased monotonically with increasing temperatures. This could be explained by the fact
that CO₂ hydrogenation becomes kinetically less favored at higher temperatures [43].

However, in the presence of sulfated-zirconia catalysts, the CO₂-to-oxygenated compounds conversions were considerably higher and followed a volcano-shape trend with a maximum at the reaction temperature of 260 °C. This observation is potentially explained by the fact that the conversion of methanol to DME increases the equilibrium conversion of CO₂

15 hydrogenation to methanol [8].

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16 Fig. 6b shows the performance of the catalysts for converting methanol to DME. 17 The ZrO₂ catalyst was found to be basically inactive for the methanol dehydration; the 18 maximum DME yield was only 0.05% at a reaction temperature of 280 °C. The 5S-ZrO₂ 19 and $10S-ZrO_2$ catalysts showed a higher yield of DME compared to the ZrO_2 catalyst. The 20 maximum DME yield for the 5S-ZrO₂ and 10S-ZrO₂ catalysts 0.5% and 1.0%, 21 respectively, was achieved at 280 °C. The catalysts with higher sulfur contents (15S-ZrO₂, 22 20S-ZrO₂ and 30S-ZrO₂) provided a greater DME yield (1.5–3.6%), and these maximum 23 conversions were achieved at a lower reaction temperature (260 °C). This suggests that the 24 formation of DME from methanol dehydration over the two groups of the catalysts may 25 have occurred on different active sites.



Figure 6 CO₂ conversion to oxygenated compounds (a), yield of DME (b) and yield of CO
(c) of the sulfated zirconia catalysts prepared with different sulfur loading contents.

4

To gain further insight on the relationship between the catalytic activity and the property of the sulfated zirconia catalysts prepared at different sulfur to zirconia ratios, we then attempted to construct a correlation between DME yield and total number of acid sites of the sulfated zirconia catalysts; the result is shown in Fig. 7. At 240 °C, the DME yield slightly increased from 0.01 to 0.43% when increasing the total number from 24 to 129 μ mol/g (i.e. the catalysts with low sulfur content). Increasing the total number of acid site from 129 to 169 μ mol/g, a dramatic increase in DME yield was observed. Similarly, the Catalysis Science & Technology Accepted Manuscript

trend was also found for the other reaction temperatures. This implies that the formation of
 DME over the sulfated zirconia catalysts with low and high sulfur contents occurs via
 different mechanisms. Further increase in the total acid sites, DME yield no longer
 changes which is mainly attributed to fast rate of methanol dehydration to DME.

5



Figure 7 Correlation of DME yield with total number of acid sites at different reaction

temperatures.

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11 Various mechanisms for the dehydration of methanol to DME have been proposed 12 and studied. Bandiera and Naccache [44] proposed that two methanol molecules adsorbed 13 simultaneously on their catalyst surface, forming two surface species $([CH_3OH_2]^+$ and 14 [CH₃O]⁻), which then condensed to form a DME and a water molecule. Kubelková et al. [45] predicted that a surface methoxy species via the protonated methanol CH₃OH₂⁺ was 15 16 initially formed and another methanol molecule reacted with the methoxyl group to 17 produce the DME product. Said et al. [32] studied the catalytic performance of sulfated 18 zirconia catalysts and interpreted the mechanism for DME formation in terms of oxidation 19 - reduction reactions in which one molecule of methanol adsorbed on an acid site and 20 another methanol molecule adsorbed on a base site, which then condensed to produce the

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DME and water. We agree that dehydration of methanol to DME occurs at dual acid-base sites but suggest that the details of the mechanism differ depending on the sulfur content of the sulfated zirconia catalysts.

4 Scheme 1 proposes the mechanism for the formation of DME from methanol 5 dehydration over the sulfated zirconia catalysts with low (0-10S) and high (15-30S) sulfur content. The proposed molecular structures and mechanism are based on characterization 6 7 analyses using FT-IR, TGA, and XANES techniques, performance test results, and 8 previous findings in the literature [32, 44, 45]. As discussed above in the FT-IR and 9 XANES results, at the low sulfur content the sulfate group preferably forms as 10 $O=S(-O-Zr)_3$ (structure A). Thus, due to the inductive effect of the sulfate group, the 11 zirconium atoms attached to the sulfate group act as a Lewis acid site for DME formation 12 [21, 32]. As the sulfur content is increased, the sulfate group forms as $-SO_4$ (structure B) 13 and seems to cover the surface of the ZrO_2 cluster. It is important to note that FT-IR and 14 XANES spectra indicate that -Zr-OH (i.e. a protonated oxygen) is present with the high 15 sulfur content catalysts only. This -Zr-OH plays a vital role in increasing DME production 16 in the presence of high $-SO_4$ coverage since the $-SO_4$ is a strong electron-withdrawing 17 group. Thus, when -SO₄ covers the ZrO₂ surface it induces the neighboring -Zr-OH to 18 become a strong Brønsted acid site, which in turns provides a proton to methanol. 19 Therefore, the methanol-to-DME reaction mechanism at low and high sulfur content 20 follows two separate pathways, as shown in Scheme 1. At low sulfur content (Pathway I), 21 one methanol molecule adsorbs on the Lewis acid site and another methanol molecule 22 adsorbs on a relatively low Lewis base site (i.e. an oxygen atom of -Zr-O-Zr-) and then 23 both undergo the reaction via $S_N 2$ transition state mechanism to produce a DME molecule 24 [46, 47]. By contrast, DME molecule creation at high sulfur content (Pathway II) [48–50] 25 takes place via the strong Brønsted acid site of -Zr-OH. In the first step, one methanol molecule adsorbs on -Zr-OH. Then, it reacts with another methanol molecule from the gas 26

1 phase via the $S_N 2$ type mechanism, resulting in a much higher DME yield than via Pathway

2 I.

Pathway I



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Structure B

Scheme 1 Proposed mechanism for the formation of DME from methanol dehydration
over the sulfated zirconia catalysts at low (pathway I) and high (pathway II) sulfur content.

7 The behavior of CO formation is shown in Fig. 6c. CO yield of all catalysts was 8 found to significantly increase with increasing temperatures. However, only small 9 difference in CO yield of all tested catalysts at each reaction temperature was observed. 10 This might be the logical consequence of the fact that the reverse water-gas shift reaction 11 proceeds very fast until equilibrium is achieved over Cu-containing catalysts [51, 52]. The 12 equilibrium is shifted towards the formation of CO with ascending temperature. This would 13 explain why all tested catalysts behave more or less the same assuming that the reaction 14 rate of the reverse water-gas shift is much faster than the formation rates of methanol and 15 dimethyl ether.

16

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1 3.3 Stability of catalysts

2 Stability is a key factor in determining whether the sulfated-zirconia materials can 3 be used as the acid catalyst for dehydration reactions in industrial production. On the basis 4 of the activity test and the proposed mechanism (Figs. 6, 7 and Scheme 1), the dehydration 5 of methanol over the sulfated zirconia catalysts consisting of low and high sulfur contents 6 provided the significant difference for DME yields. Therefore, the stability of the two 7 groups of the catalysts was investigated, 10S-ZrO₂ and 20S-ZrO₂ catalysts representing low 8 and high sulfur coverage, respectively, with pure ZrO_2 and H-ZSM-5 used as the reference. 9 Before initiating the experiment, a suitable testing condition must be considered. This is 10 because the direct synthesis of DME from CO₂ hydrogenation requires two functional 11 catalysts: the CuO-ZnO-ZrO₂ catalyst and the sulfated zirconia catalyst. Note that these two 12 catalysts can be deactivated over time. Generally, the deactivation of the Cu-based catalyst 13 for methanol synthesis from CO_2 hydrogenation is caused by the loss of copper surface 14 area due to the low Tammann temperature of copper and the exothermicity of the reaction 15 [53, 54]. In order to assess the real performance of the sulfated zirconia catalyst without the 16 imposition from the CuO-ZnO-ZrO₂ catalyst, the stability test must be performed under a 17 condition that can maintain a constant yield of methanol.

18 Fig. 8 shows the STY versus the time-on-stream of DME and methanol over four 19 catalysts: CuO-ZnO-ZrO₂/ZrO₂, CuO-ZnO-ZrO₂/10S-ZrO₂, CuO-ZnO-ZrO₂/20S-ZrO₂ and 20 CuO-ZnO-ZrO₂/H-ZSM-5. The STY of methanol over all catalyst systems was found to be 21 almost constant during the 75 h experiment. This indicated that the methanol catalyst 22 (CuO-ZnO-ZrO₂) had an excellent stability. Regarding the STY of DME, the CuO-ZnO-23 $ZrO_2/10S-ZrO_2$ catalyst showed a substantial decrease in DME yield ca. 41.7% during the 24 75 h time-on-stream experiment, while the CuO-ZnO-ZrO₂/20S-ZrO₂ catalyst exhibited 25 much greater durability, experiencing only a 16.9% reduction under the identical reaction 26 condition. Saravanan et al. [28] reported two possible reasons for the successive decrease

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1 in the activity of the sulfated zirconia catalysts: poisoning by water molecules formed 2 during the reaction, and leaching of sulfate species from the catalyst in the polar alcohol 3 medium. According to the mechanism we proposed above, for the catalyst with low sulfur content (10S-ZrO₂), the methanol dehydrated over Lewis acid-base sites. This is in 4 5 harmony with the direct synthesis of DME from CO_2 hydrogenation, which produces a large amount of water when compared to either the methanol dehydration or the one-step 6 7 synthesis of DME from syngas [31, 32]. This created water is the major cause of the 8 poisoning at the active sites of the catalysts, since the water molecule competes with the methanol molecule for adsorption onto the Lewis acid sites (Zr^{4+}) . This is a reason the 9 10 reduction of STY of DME over time is observed and this catalyst provides the maximum 11 yield of DME at the higher reaction temperature (Fig. 6b). When the reaction temperature 12 is increased, the desorption of the water molecules may regenerate the catalyst activity. By 13 contrast, the 20S-ZrO₂ catalyst is mainly composed of Brønsted acid sites, which were 14 slightly affected by the water [28]. Therefore, the deactivation rate of the 20S-ZrO₂ catalyst 15 was much lower than that of the 10S-ZrO₂ catalyst.

16 CuO-ZnO-ZrO₂ catalysts are commonly deactivated through sulfur poisoning, but 17 we observed no signs of deactivation of our CuO-ZnO-ZrO₂ catalyst. One of the following 18 three hypotheses could explain the durability of this particular Cu-based catalyst. (1) Since 19 the sulfated zirconia – an acid catalyst which was mixed with Cu-ZnO-ZrO₂, a methanol 20 conversion catalyst, to form our catalytic system - was calcined at 550 °C for 2 h, and, as a 21 result, only the stable form of the sulfate remained on the zirconia surface, sulfate ions are 22 not transferred from the sulfated zirconia to the Cu-ZnO-ZrO2 and therefore do not 23 deactivate it. During the experiment, water and methanol are produced, but they cannot 24 leach out sulfate ions, so that there is no sulfur source to poison the Cu-based catalyst. (2) 25 The presence of ZnO in the catalyst improves sulfur resistance by forming 26 thermodynamically stable ZnS [9], so that the few sulfate ions that may have been leached

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out from the sulfated zirconia surface during the reaction are eliminated by the Zn and the activity of the Cu-based catalyst remains constant. (3) While the leaching process of sulfate ions is the major cause of the sulfated zirconia deactivation, the Cu-based catalyst exhibits excellent stability because the sulfate ions are not changed to H_2S , the most active form for poisoning a metal catalyst. [Note: the spent catalyst should be further characterized for a better understanding of the deactivation phenomena, e.g., coke deposition and leaching of sulfate ions.]

8 A benchmark between the new catalyst and a commercial catalyst is required to 9 allow a straightforward comparison. In the present case, the stability of the $20S-ZrO_2$ 10 catalyst is compared to that of the H-ZSM-5 catalyst, as demonstrated in Fig. 8c. The STY 11 of DME over the $20S-ZrO_2$ catalyst was found to be higher than that of the H-ZSM-5 12 catalyst at the beginning of the experiment, indicating that the $20S-ZrO_2$ catalyst was more 13 active. However, the $20S-ZrO_2$ catalyst exhibited a rapid decrease in the STY of DME 14 while the STY of DME of the H-ZSM-5 slightly decreased at approximately 2.85% of 75 h 15 on stream, which was significantly lower than that of the $20S-ZrO_2$ catalyst (16.9 %). This 16 indicates that the sulfated zirconia catalysts cannot be considered for the practical catalyst 17 at this stage since they cannot compete with the commercial H-ZSM-5 catalyst when 18 considered the long-term stability. However, given that the stability of the sulfated zirconia 19 catalyst is improved, it might be considered a good industrial acid catalyst due to its 20 elevated activity and ease of preparation.



Figure 8 Space-time yields of methanol and DME as a function of time-on-stream of CuO-

3 ZnO-ZrO₂/ZrO₂ (a), CuO-ZnO-ZrO₂/10S-ZrO₂ (b), and CuO-ZnO-ZrO₂/20S-ZrO₂ and 4

CuO-ZnO-ZrO₂/H-ZSM-5 (c).

Reaction conditions: $T = 260 \text{ }^{\circ}\text{C}$, P = 2 MPa, Flow rate = 60 mL/min. 5

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7 4. Conclusions

8 The physicochemical properties, activity and stability of the sulfated zirconia 9 catalysts were strongly affected by the sulfur content on the zirconia surface. At low sulfur 10 content (5S-ZrO₂ and 10S-ZrO₂), the tridentate sulfate formed on the zirconia surface and 11 induced zirconia atoms to act as weak Lewis acid sites. These catalysts were active for 12 methanol dehydration at relatively high reaction temperatures. At high sulfur contents 13 $(15S-ZrO_2, 20S-ZrO_2)$ and $30S-ZrO_2)$, a protonated sulfate species formed and donated a 14 significant Brønsted acidity, which efficiently catalyzed the methanol dehydration even at 15 relatively low reaction temperatures. In addition, the catalysts with high sulfur content 16 showed a much greater stability than those with low sulfur contents because water 17 molecules preferentially adsorbed on the Lewis acid sites. It was also demonstrated that 18 Brønsted acidity is essential important for the direct synthesis of DME from CO_2 19 hydrogenation. This finding may open up a new application for sulfated zirconia catalysts

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hydrogenation that could lead to a sustainable fuel in the future.

(combined with Cu-based catalysts) in the direct synthesis of DME from CO_2

- 7 8 9 10 11 12 13 measurement. Reference Rev., 2014, 43, 7995-8048. Technol. 2014, 119, 286–304.
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- 15

- 17 1. D. L. Royer, R. A. Berner and J. Park, Nature, 2007, 446, 530-532.
- 18 2. A. Goeppert, M. Czaun, J.-P. Jones, G. K. S. Prakash and G. A. Olah, Chem. Soc. 19
- 3. O. Martin and J. Pérez-Ramírez, Catal. Sci. Technol., 2013, 3, 3343–3352. 20
- 21 4. E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal and J. Pérez-Ramírez, 22 Energy. Environ. Sci., 2013, 6, 3112–3135.
- 23 5. K. Sato, Y. Tanaka, A. Negishi and T. Kato, J. Power Sources, 2012, 217, 37–42.
- 24 6. T. H. Fleisch, A. Basu and R. A. Sills, J. Natural Gas Sci. Eng., 2012, 9, 94–107.
- 25 7. G. Thomas, B. Feng, A. Veeraragavan, M. J. Cleary and N. Drinnan, Fuel Process. 26

Catalysis Science & Technology Accepted Manuscript

1	8. WJ. Shen, KW. Jun, HS. Choi and KW. Lee, Korean J. Chem. Eng., 2000,
2	17, 210–216.
3	9. M. V. Twigg and M. S. Spencer, Appl. Catal. A: Gen., 2001, 212, 161–174.
4	10. O. Oyola-Rivera, M. A. Baltanás and N. Cardona-Martínez, J. CO ₂ Util., 2015, 9, 8-
5	15.
6	11. F. Studt, I. Sharafutdinov, F. Abild-Pedersen, C. F. Elkjær, J. S. Hummelshøj, S.
7	Dahl, I. Chorkendorff and J. K. Nørskov, Nat. Chem., 2014, 6, 320-324.
8	12. F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro and F. Frusteri, J. Catal.,
9	2007, 249 , 185–194.
10	13. G. Wengui, W. Hua, W. Yuhao, G. Wei and J. Miaoyao, J. Rare Earth., 2013, 31,
11	470–476.
12	14. Y. Zhang, D. Li, Y. Zhang, Y. Cao, S. Zhang, K. Wang, F. Ding and J. Wu, Catal.
13	<i>Commun.</i> , 2014, 55 , 49–52.
14	15. D. Mao, J. Xia, B. Zhang and G. Lu, Energy Convers. Manage., 2010, 51, 1134-
15	1139.
16	16. T. Takeguchi, KI. Yanagisawa, T. Inui and M. Inoue, Appl. Catal. A: Gen., 2000,
17	192 , 201–209.
18	17. V. Vishwanathan, KW. Jun, JW. Kim and HS. Roh, Appl. Catal. A: Gen.,
19	2004, 276 , 251–255.
20	18. D. Mao and X. Guo, <i>Energy Technol.</i> 2014, 2 , 882–888
21	19. G. Bonura, M. Cordaro, C. Cannilla, F. Arena and F. Frusteri, Appl. Catal. B:
22	<i>Environ.</i> , 2014, 152–153 , 152–161.
23	20. H. Ban, C. Li, K. Asami and K. Fujimoto, Catal. Commun., 2014, 54, 50-54.
24	21. G. D. Yadav and J. J. Nair, Micropor. Mesopor. Mater., 1999, 33, 1-48.
25	22. X. Li, K. Nagaoka and J. A. Lercher, J. Catal., 2004, 227, 130-137.

1	23. G. A. Urzhuntsev, E. V. Ovchinnikova, V. A. Chumachenko, S. A. Yashnik, V. I.
2	Zaikovsky and G. V. Echevsky, Chem. Eng. J., 2014, 238, 148-156.
3	24. M. A. Ahmed, Fuel Process. Technol., 2011, 92, 1121–1128.
4	25. G. D. Yadav and A. D. Murkute, J. Catal., 2004, 224, 218–223.
5	26. Y. Zhang, W. – T. Wong and K. – F. Yung, Appl. Energy, 2014, 116, 191–198.
6	27. M. L. Grecea, A. C. Dimian, S. Tanase, V. Subbiah and G. Rothenberg, Catal. Sci.
7	<i>Technol.</i> , 2012, 2 , 1500–1506.
8	28. K. Saravanan, B. Tyagi and H. C. Bajai, Catal. Sci. Technol., 2012, 2, 2512–2520.
9	29. M. Popova, Á. Szegedi, A. Ristić and N. N. Tušar, Catal. Sci. Technol., 2014, 4,
10	3993–4000.
11	30. M. Waqif, J. Bachelier, O. Saur and J C. Lavalley, J. Mol. Catal., 1992, 72, 127-
12	138.
13	31. F. S. Ramos, A. M. Duarte de Farias, L. E. P. Borges, J. L. Monteiro, M. A. Fraga, E.
14	F. Sousa-Aguiar and L. G. Appel, Catal. Today, 2005, 101, 39-44.
15	32. A. EA. A. Said, M. M. A. El-Wahab, M. A. El-Aal, J. Mol. Catal. A: Chem., 2014,
16	394 , 40–47.
17	33. N. A. Khan, D. K. Mishra, I. Ahmed, J. W. Yoon, JS. Hwang and S. H. Jhung,
18	Appl. Catal. A: Gen., 2013, 452, 34–38.
19	34. A. Osatiashtiani, A. F. Lee, D. R. Brown, J. A. Melero, G. Morales and K. Wilson,
20	Catal. Sci. Technol., 2014, 4, 333–342.
21	35. Y. Sun, S. Ma, Y. Du, L. Yuan, S. Wang, J. Wang, F. Deng and FS. Xiao, J. Phys.
22	Chem. B, 2005, 109, 2567–2572.
23	36. C. Morterra, G. Cerrato, G. Meligrana, M. Signoretto, F. Pinna and G. Strukul, Catal.
24	Lett., 2001, 73 , 113–119.
25	37. F. Haase and J. Sauer, J. Am. Chem. Soc., 1998, 120, 13503-13512.

Catalysis Science & Technology Accepted Manuscript

1	38. X. Dou, D. Mohan, C. U. Pittman Jr. and S. Yang, Chem. Eng. J., 2012, 198-199,
2	236–245.
3	39. SY. Chen, LY. Jang and S. Cheng, J. Phys. Chem. B, 2006, 110, 11761 – 11771.
4	40. C. Liu, T. Bolin, P. Northrup, S. Lee, C. McEnally, P. Kelleher, L. Pfefferle and G.
5	L. Haller, Top. Catal., 2014, 57, 693-705.
6	41. C. Liu, L. D. Pfefferle and G. L. Haller, Top. Catal., 2014, 57, 774–784.
7	42. S. Pin, T. Huthwelker, M. A. Brown and F. Vogel, J. Phys. Chem. A, 2013, 117,
8	8368–8376.
9	43. Y. Zhang, Q. Sun, J. Deng, D. Wu and S. Chen, Appl. Catal. A: Gen., 1997, 158,
10	105–120.
11	44. J. Bandiera and C. Naccache, Appl. Catal., 1991, 69, 139–148.
12	45. L. Kubelková, J. Nováková and K. Nedomová, J. Catal., 1990, 124, 441–450.
13	46. S. R. Blaszkowski and R. A. van Santen, J. Am. Chem. Soc., 1996, 118, 5152-5153.
14	47. H. Yang, H. Song, H. Zhang, P. Chen, Z. Zhao, J. Mol. Catal. A: Chem., 2014, 381,
15	54–60.
16	48. B. C. Gates and L. N., Johanson, J. Catal. 1969, 14, 69-76.
17	49. P. K. Kiviranta-Pääkkönen and L. K. Struckmann, Ind. Eng. Chem. Res. 1998, 37,
18	18–24.
19	50. S. Hosseininejad, A. Afacan and R. E. Hayes, Chem. Eng. Res. Des. 2012, 90, 825-
20	833.
21	51. J. Yoshihara and C. T. Campbell, J. Catal., 1996, 161, 776–782.
22	52. T. Tagawab, G. Pleizier and Y. Amenomiya, Appl. Catal., 1985, 18, 285–293.
23	53. F. S. R. Barbosa, V. S. O. Ruiz and J. L. F. Monteiro, Catal. Lett., 2008, 126, 173-
24	178.
25	54. T. Witoon, T. Permsirivanich, W. Donphai, A. Jaree and M. Chareonpanich, Fuel
26	Process. Technol., 2013, 116, 72–78.

Pathway I



Methanol can be dehydrated to form DME over the sulfated zirconia catalysts via pathway I, if the sulfur content is low, and pathway II, if the sulfur content is high.