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CO_2 hydrogenation to methanol at high reaction temperatures over In_2O_3/ZrO_2 catalysts: Influence of calcination temperatures of ZrO_2 support

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Highlights

- In₂O₃/ZrO₂ catalysts are prepared with different calcination temperatures of ZrO₂.
- Increasing calcination temperatures strengthen the adsorption of CO₂ and H₂ on the catalysts surface.
- Adsorption strength of CO₂ and H₂ determines the formation of CH₃OH.
- Weak adsorption strength facilitates the formation of CH₄.
- Strong adsorption strength enhances the formation of CH₃OH.

Abstract

This work investigated the role of calcination temperatures (600, 700, 800, 900 and 1000 °C) of ZrO₂ support on the physicochemical properties of In₂O₃/ZrO₂ catalysts (denoted as 20In/Zr-X with X, calcination temperature of ZrO₂ support) as well as their catalytic activity in CO₂ hydrogenation to methanol at high reaction temperatures (320– 400 °C). The calcination temperature played a crucial role on crystal structure of In₂O₃ and ZrO₂, reducibility of In₂O₃ and adsorption-desorption of CO₂ and H₂. XRD analysis revealed that cubic In₂O₃ and amorphous ZrO₂ were presented in 20In/Zr-600. With increasing calcination temperature of ZrO₂ support from 600 to 1000 °C, the tetragonal ZrO₂ was formed and the In₂O₃ and ZrO₂ crystallite sizes were enlarged. The degree of In₂O₃ reduction was found to gradually decrease with increasing the calcination temperature of ZrO₂ support due to the increase of In₂O₃ crystallite size. The adsorption strength of CO₂ and H₂ with the catalysts surface was found to be as follows: $ZrO_2 >$ $20In/Zr-1000 > 20In/Zr-900 > 20In/Zr-800 > 20In/Zr-700 > 20In/Zr600 > In_2O_3$. The different calcination temperatures of ZrO₂ support did not significantly affect the formation of CO but strongly dominated the yield of CH₃OH and CH₄. At reaction temperatures of 320–340 °C, the 20In/Zr-800 provided the maximum yield of CH₃OH. However, as the reaction temperature was further increased, the maximum yield of CH₃OH was obtained over the 20In/Zr-900, indicating that higher adsorption strength of

 CO_2 and H_2 enhanced the formation of CH_3OH at higher reaction temperatures. Moreover, the strong interaction of H_2 and CO_2 with the catalysts surface suppressed the formation of CH_4 .

Keywords: CO₂ hydrogenation; Light olefins; Methanol; Calcination temperature; In₂O₃/ZrO₂

1. Introduction

With the continually escalating world's energy demand derived from rapid growth of population and economic advancement, an ever-increasing exploitation of carbon-rich fossil fuels in industry, transportation, and buildings has emitted large amounts of CO₂ into the atmosphere which allegedly contributes significantly to global warming and extreme climate change. As a result, mitigating CO₂ emissions is in urgent need. Among the potential approaches assessed for reducing CO₂, the utilization of CO₂ as a feedstock for the production of fuels and commercially important chemicals, preferably light olefins (ethylene, propylene and butylene) which are key platform molecules for the chemical industry has gained enormous attention [1-5]. In general, light olefins are mainly generated from cracking of petroleum-based naphtha, which is non-eco-friendly and energy-intensive process [6]. The transformation of CO₂ into light olefins is therefore more capable of creating a carbon-neutral chemicals cycle and economic feasibility in response to the increasing their global demands simultaneously with the dwindling of fossil fuel resources.

Intense research efforts have been conducted to produce light olefins from CO₂ hydrogenation via modified Fischer-Tropsch synthesis (FTS), which consists of two step processes. A first step is the formation of CO through the reverse water–gas shift (RWGS) reaction, followed by the further transformation of CO into hydrocarbons via

FTS [2,7-9]. However, this process suffers from wide distribution of hydrocarbons products which becomes an obstruction to fulfill the requirement for commercial production and applications in large-scale industry. Alternatively, methanol synthesis from CO₂ hydrogenation coupled *in situ* with methanol to olefins reaction is approved for achieving high selectivity to C₂–C₄ hydrocarbons (>80%) [10-13]. In this route, CO₂ is initially hydrogenated to methanol and subsequently converted to low-carbon olefins through the methanol-to-olefins (MTO) process. This route requires the hybrid catalysts possessing both active components for methanol synthesis and methanol-to-olefins conversion. Due to the fact that the MTO process is efficiently operated in the vapor phase at reaction temperature of 340–540 °C, the conventional Cu-based catalysts which are highly active and selective for methanol synthesis from CO₂ hydrogenation at only temperature of 220–250 °C cannot be used for the direct CO₂-to-light olefins hydrogenation.

Recently, In₂O₃-based catalysts have shown superior catalytic performance with high activity, selectivity and remarkable stability in the direct synthesis of methanol from CO₂/CO at high reaction temperatures (280–330 °C) [14-16], and the positive effect of ZrO₂ support on the catalytic activity of In₂O₃/ZrO₂ catalyst was reported [16,17]. In₂O₃ supported on ZrO₂ could dramatically increase methanol yield by promoting the reduction of Zr⁴⁺ to Zr³⁺ at the interface between In₂O₃ and ZrO₂, resulting in the creation of oxygen vacancy which was able to bind the key intermediates for the methanol formation. Previous studies demonstrated that structural aspects of catalysts have considerable affected by calcination temperature and thereby altered the interaction between metal oxides and the catalyst supports which contributed to enhance the catalytic performance [18-20]. High isobutanol selectivity was achieved from CO hydrogenation over the K-ZrO₂/Cu/Al₂O₃ catalyst calcined at an optimized temperature, which was

attributed to the synergy effect between Cu and ZrO₂. Meanwhile, the CuAlO₂ phase formed over K-Cu/Al₂O₃ catalyst calcined at high temperature (900 °C) was responsible for ethanol formation [21]. Moreover, the significance of calcination temperature was also illustrated over K-Cu/ZrO₂-La₂O_{3(x)} catalyst [22] and Mn/Cu/ZrO₂ catalyst [23]. Similarly, the calcination temperature has a substantial influence on the surface textural properties and phase structure of Cu/ZrO₂ catalyst. The Cu/amorphous-ZrO₂ (a-ZrO₂) prepared by calcination at low temperature (350 °C) exhibited higher methanol productivity in CO₂/CO hydrogenation than those on Cu/tetragonal-ZrO₂ (t-ZrO₂) and Cu/monoclinic-ZrO₂ (m-ZrO₂) which attained from the higher calcination temperature [24,25]. This result was attributed to the presence of more suitable interfacial sites between Cu and a-ZrO₂. Based on the study of Wu [26], the strong interaction between Pd and ZrO₂ support was favored by the phase transformation of t-ZrO₂ to m-ZrO₂ which related to the pretreated temperature and thus increased the activity in methane oxidation.

Until now, the effect of calcination temperature of ZrO_2 support on the physicochemical properties of In_2O_3/ZrO_2 catalysts and their catalytic activity for the hydrogenation of CO₂ to methanol at high reaction temperatures (320–400 °C) has not yet been investigated. In the present study, aiming for increasing methanol yield at high reaction temperature, a series of In_2O_3/ZrO_2 catalysts with varied calcination temperatures of ZrO_2 support were prepared and the structure-activity relationship of In_2O_3/ZrO_2 catalysts was studied.

2. Experimental

2.1. Preparation of ZrO₂ supports

A cetyltrimethylamonium bromide (CTAB)-assisted precipitation technique was applied for the synthesis of ZrO₂ support. Briefly, 0.1M ZrOCl₂·8H₂O aqueous solution

was mixed with 0.1M solution of CTAB and stirred at room temperature for 15 min. Afterwards, the pH of the homogeneous mixed solution was adjusted by adding 25% ammonia solution under vigorous stirring until pH value was reached to 11.5 for precipitating zirconium as Zr(OH)₄. After aging at room temperature for 1 h and then at 60°C for 94 h, the precipitate was filtered and exhaustively washed with deionized water and ethanol several times. Finally, the resulting product was dried at 60 °C for 20 h prior to calcination in air at different temperatures (600, 700, 800, 900 and 1000 °C) for 2 h with a heating rate of 2 °C/min. The obtained products were designated as Zr-600, Zr-700, Zr-800, Zr-900 and Zr-1000, respectively.

2.2. Synthesis of In₂O₃/ZrO₂ catalysts

In₂O₃ was supported on ZrO₂ by incipient wetness impregnation method started by impregnating ZrO₂ with desired amount (20 wt% of In) of an aqueous solution of In(NO₃)₃·xH₂O and subsequent drying at 100 °C overnight and calcination at 450 °C for 2 h. The resulting catalysts were denoted as 20In/Zr-X, in which X was the calcination temperature of ZrO₂ support.

2.3. Catalyst characterization

Phase and crystalline structure of all In₂O₃/ZrO₂ catalysts were analyzed by powder X-ray diffraction (XRD) performed on a Bruker D-8 Advance diffractometer, applying Cu K α radiation (λ =0.154056 nm) source. The data were collected with a scanning step length of 0.02° over the scattering angles (2 θ) ranging from 10° to 75°.

To analyze BET surface area, pore size distribution and pore volume of the catalysts, N₂ physisorption was measured with a Micromeritics Instrument (3Flex Surface Model) at -196 °C. Prior to measurement, the samples were degassed at 200 °C for 12 h

to remove any moisture. The apparent BET surface area was estimated from the adsorption isotherms at a relative pressure (P/P^0) between 0.05 and 0.3 by employing the Brunauer–Emmet–Teller (BET) equation. The pore size distribution was assessed according to the Barrett–Joyner–Halenda (BJH) method based on the adsorption branch of the isotherms.

Reducibility of the catalysts was investigated by H₂ temperature-programmed reduction (H₂-TPR) in a continuous-flow fixed-bed tubular reactor equipped with a thermal conductivity detector (TCD). 100 mg of catalyst was loaded into a quartz tube and heated from room temperature to 900 °C in 9.6% H₂/Ar gas mixture (30 mL min⁻¹) with a heating ramp rate of 10 °C min⁻¹ and the consumption of H₂ was monitored by TCD.

The evolution of In species during reduction stage with H₂ at 50-400 °C was investigated by time-resolved X-ray absorption spectroscopy (TR-XAS) at Beamline 5.2 (SUT-NANOTEC-SLRI) of the Synchrotron Light Research Institute (SLRI), Thailand which operated at 1.2 GeV and 50-150 mA. The energy was selected with a Ge (220) crystal monochromator and the edge energy (E₀) of metallic In was determined from the standard materials (3730.1 eV). In each experiment, the catalyst sample was first pretreated under O₂ flow (30 mL min⁻¹) at 150 °C for 20 min to remove pre-adsorbed molecules, followed by heating to 300 °C at a rate of 2 °C min⁻¹ with 66.67% H₂/N₂ gas mixture (22.5 mL min⁻¹). After maintaining for 1 h, the temperature was raised again to 400 °C with the rate of 2 °C min⁻¹. The XANES spectra of In L3-edge collected in transmission mode was processed and fit to the linear relation for quantifying the amounts of In by using ATHENA and ARTEMIS software.

To examine the adsorption-desorption behavior of H_2 and CO_2 on the surface of In_2O_3/ZrO_2 catalysts, temperature programmed desorption of H_2 and CO_2 (H_2 and CO_2 -

TPD) were carried out using the same apparatus employed in H₂-TPR measurement. Prior to acquiring the adsorption-desorption, the catalyst was *in-situ* activated in 9.6% H₂/Ar flow (60 mL min⁻¹) at 300 °C for 1 h. After cooling to 50 °C, 9.6% H₂/Ar or 33.3% CO₂/Ar gas flow was adsorbed and equilibrated over the catalyst for 1 h. Then, the catalyst was purged with Ar flow for 1 h to remove all physisorbed molecules. The TPD experiment was started by increasing catalyst bed temperature from 50 °C to 900 °C at a ramp rate of 5 °C min⁻¹ under pure Ar flow, and the desorbed H₂ and CO₂ was monitored quantitatively by a TCD.

The nanostructures of catalysts were examined with transmission electron microscopy (TEM: JEOL-2010 microscope at 200 kV)

2.4. Catalytic activity test

The catalytic performance of the catalysts was carried out in a fixed-bed continuous-flow reactor operated in down-flow mode under high pressure. In brief, 0.5 g of each In₂O₃/ZrO₂ catalyst was contained in the stainless steel tube reactor. Prior to reaction, the catalyst was *in situ* reduced in flowing H₂ of 60 mL min⁻¹ at 300 °C for 1 h and then the reactant gas mixture with a CO₂/H₂/N₂ stoichiometric ratio of 1:3:1 (75 mL min⁻¹) was introduced into the reactor. The temperature of the catalyst bed was increased to the designated reaction temperature of 320, 340, 360, 380 and 400 °C and the pressure was regulated to 20 bar. The effluent gas was analyzed by GC-14B and GC 8A gas chromatography analyzer equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID), respectively. A Shin Carbon ST column attached to the TCD was used to separate CO₂, CO, H₂ and N₂, while hydrocarbon and oxygenated products were detected with the FID using a Chromosorb WAW (20% PEG) column. CO₂ conversion, selectivity and yields of products were calculated by mass balance.

3. Results and discussion

3.1. Catalysts characterization

Figure 1 shows the XRD patterns of 20 wt% In loaded on ZrO_2 supports of which the ZrO₂ supports were calcined at different temperatures including 600 °C (20In/Zr-600), 700 °C (20In/Zr-700), 800 °C (20In/Zr-800), 900 °C (20In/Zr- 900) and 1000 °C (20In/Zr-1000). The 20In/Zr-600 showed the diffraction lines at 20 values of 30.586, 35.463, 51.025 and 60.669° which were indexed of In₂O₃ with a cubic bixbyite phase [11]. No diffraction line of ZrO₂ was visible at calcination temperature of 600 °C, suggesting the presence of amorphous ZrO₂. Increasing calcination temperature of ZrO₂ support from 600 to 700 °C led to the appearance of diffraction lines at 20 values of 30.210, 35.248, 50.201 and 60.165° which could be assigned to tetragonal ZrO₂ phase [27]. With further increasing calcination temperatures from 700 to 1000 °C, the intensity of diffraction lines of both In₂O₃ and tetragonal ZrO₂ phases became more pronounced, indicating larger In₂O₃ and ZrO₂ crystallite sizes.



Figure 1 XRD patterns of In_2O_3/ZrO_2 catalysts prepared with different calcination temperatures of ZrO_2 support, while the In content is fixed at 20 wt%.

Figure 2a shows the N₂-sorption isotherms of different In₂O₃/ZrO₂ catalysts. The N₂-sorption isotherms of all catalysts were found to be type IV with H₂ hysteresis loop which was a characteristic of mesoporous materials with an ink-bottle structure. The adsorption branch was used to calculate the pore size distribution according to BJH method. As shown in Figure 2b, all catalysts showed the pore size distribution in the range of 2–20 nm. It can be clearly seen that small mesoporosity (2-5 nm) gradually decreased with increasing calcination temperature of the ZrO₂ support, which was attributed to the sintering of small ZrO₂ crystallite size. Accordingly, the average pore size increased accompanied by the reduction of BET surface area and total pore volume as the calcination temperature was increased (Table 1).



Figure 2 N₂ sorption isotherms of In_2O_3/ZrO_2 catalysts prepared with different calcination temperatures of ZrO_2 support, while the In content is fixed at 20 wt%.

Figure 3 shows the reducibility of In₂O₃, ZrO₂ and 20 wt% In loaded on ZrO₂ supports calcined at different temperatures. The H₂ consumption of ZrO₂ support began at temperature above 450 °C. As the reaction temperatures were in the range of 320–400 °C, the ZrO₂ support was not reduced under the investigated conditions. In contrast to ZrO₂ support, the bare In₂O₃ showed two H₂ consumption peaks related to the reduction of In₂O₃ at different locations. The low-temperature feature (150–300 °C) was attributed to a surface reduction of In₂O₃, while the high-temperature feature (400–800 °C) belonged to reduction of bulk In₂O₃ [28]. In comparison to the bare In₂O₃, the impregnation of In₂O₃ onto the ZrO₂ support led to a shift of onset H₂ consumption to a higher temperature, suggesting an interaction of In₂O₃ and ZrO₂.



Figure 3 H₂-TPR profiles of In_2O_3/ZrO_2 catalysts prepared with different calcination temperatures of ZrO_2 support, while the In content is fixed at 20 wt%.

The *in situ* time-resolved X-ray absorption near edge spectroscopic (TR-XANES) examination of the catalysts collected during reduction under identical experimental condition could provide additional insight into the evolution of phase transformation of In species as shown in Figure 4. The In L3-edge XANES spectra of In foil exhibited adsorption edge energy and white line energy at 3735 eV and 3747 eV, respectively which were lower than that for In₂O₃ (adsorption edge energy of 3740 eV and white line energy of 3758 eV). It can be seen that the XANES spectra at In L3-edge for all In₂O₃/ZrO₂ catalysts measured at 50 °C showed notably higher adsorption edge energy than In foil, and were slightly lower than that of In₂O₃. For 20In/Zr-600 catalyst, a gradual shift toward lower edge energy position was attained after expose to reducing gas (H₂) at 275 °C, while a clear decrease in the white line intensity could also be observed. Further rise in reduction temperature led to the predominant decline in white line intensity, indicating a reduction in the oxidation state of the In species. For In₂O₃/ZrO₂

catalysts calcined at higher temperatures (700-1000 °C), the observed spectral changes were quite similar to those of the 20In/Zr-600 catalyst. However, it could be noted that the decreasing trend in white line intensity with increasing reduction temperature was less pronounced when the catalysts were prepared at higher calcination temperatures of ZrO₂ (20In/Zr-800, 20In/Zr-900 and 20In/Zr-1000), suggesting the harder reducibility of In species due to the larger In₂O₃ crystallite size over the ZrO₂ support calcined at higher temperatures. The percentage of metallic In analyzed by the linear combination fitting (LCF) of the difference TR-XANES spectra were plotted in Figure 5 as a function of reduction temperatures (275-400 °C). The metallic In content obtained at 275 °C was found to be as follows: 20In/Zr-600 (14.8%) > 20In/Zr-700 (13.7%) > 20In/Zr-800 (13.6%) > 20In/Zr-900 (7.8%) > 20In/Zr-1000 (5.7%). As can be seen, a similar observation in the increase of metallic In content with increasing reduction temperature from 275 °C to 400 °C could be observed for all catalysts prepared with different calcination temperature of ZrO₂. The highest metallic In content of 14.8-44.8% were achieved over the catalyst calcined at 600 °C (20In/Zr-600), which were approximately 2.5–3 times higher than 20In/Zr-1000 catalyst.



Figure 4 Time-resolved X-ray absorption spectroscopy spectra of different In_2O_3/ZrO_2 catalysts during reduction with H₂ at different temperatures.



Figure 5 In content as a function of reduction temperature for different In_2O_3/ZrO_2 catalysts.

The H₂ desorption profiles of pre-reduced In₂O₃, ZrO₂, and different In₂O₃/ZrO₂ catalysts are presented in Figure 6. The H₂-TPD profile of pre-reduced In₂O₃ exhibited the onset temperature at 150 °C and appeared two desorption peaks. The low-temperature peak (275 °C) could be ascribed to weakly adsorbed H₂ species, while the high-temperature peak (600 °C) could be attributed to a strong adsorption of atomic H species. In contrast to In₂O₃, the pre-reduced ZrO₂ displayed only one broad desorption peak with the onset temperature of 250 °C. Clearly, the area under the H₂-TPD of the pre-reduced ZrO₂ was considerably lower than that of the pre-reduced In₂O₃, indicating the low H₂ adsorption capacity over the pre-reduced ZrO₂. The H₂-TPD profile of all In₂O₃/ZrO₂ catalysts showed their desorption peaks between the desorption peak of low-temperature feature of the In₂O₃ and that of ZrO₂, indicating an interfacial contact between In₂O₃ and ZrO₂ which modified the electronic properties of In₂O₃/ZrO₂ catalysts compared to the bare In₂O₃ and ZrO₂. Regarding to the desorption peak of all materials,

the order of interaction of H₂ with the surface of materials was found to be as follows: $ZrO_2 > 20In/Zr-1000 > 20In/Zr-900 > 20In/Zr-800 > 20In/Zr-700 > 20In/Zr600 > In_2O_3.$



Figure 6 H₂-TPD profiles of In₂O₃, ZrO₂ and In₂O₃/ZrO₂ catalysts prepared with different calcination temperatures of ZrO₂ support, while the In content is fixed at 20 wt%.

Figure 7 shows the CO₂-TPD profiles of pre-reduced In₂O₃, ZrO₂, and different In₂O₃/ZrO₂ catalysts. The CO₂-TPD profile over the pre-reduced In₂O₃ showed two distinct desorption peaks affirming two different active sites on the surface of In₂O₃ which were likely associated with the presence of metallic In and oxygen vacancy of In₂O₃. In comparison to bare In₂O₃, the CO₂-TPD profile of bare ZrO₂ also exhibited two desorption peaks but their desorption peak shifted towards higher temperatures, indicating the stronger interaction of CO₂ on the ZrO₂ surface. The CO₂-TPD profile of 20In/Zr-600 displayed a combination of that of bare In₂O₃ and ZrO₂. Moreover, the intensity of CO₂-TPD profile in the temperature range of 250–400 °C of 20In/Zr-600 was

higher than that of bare In_2O_3 and ZrO_2 , suggesting that the interfacial contact of In_2O_3 and ZrO_2 particles to be acted as the active site. Similar to the H₂-TPD analysis, increasing calcination temperature of ZrO_2 support led to a gradual increase in CO_2 adsorption strength.



Figure 7 CO₂-TPD profiles of In_2O_3 , ZrO_2 and In_2O_3/ZrO_2 catalysts prepared with different calcination temperatures of ZrO_2 support, while the In content is fixed at 20 wt%.

3.2. Catalytic activity test for CO_2 hydrogenation over different In_2O_3/ZrO_2 catalysts

The catalytic performance of the different In_2O_3/ZrO_2 catalysts in the CO₂ hydrogenation reaction was evaluated in a fixed-bed reactor operated in the temperature range of 320–400 °C and pressure of 20 bar. The influence of calcination temperature of ZrO₂ support was assessed in the aspect of the evolution of CO₂ conversion along with product yields by keeping weight percent of In loading constant (20 wt.%). For all

In₂O₃/ZrO₂ catalysts, only three carbon-containing products including CH₃OH, CO and CH₄ were found. CH₃OH and CO were generated by hydrogenation of CO₂ to methanol (reaction (1)) and reverse water-gas shift reaction (reaction (2)), respectively, while CH₄ was possibly formed by CO methanation (reaction (3)) and/or the hydrogenolysis of CH₃OH to CH₄ (reaction (4)).

$\rm CO_2 + 3H_2 \leftrightarrow \rm CH_3OH + H_2O$	$\Delta H^{\circ} = -49.4 \mathrm{kJ} \mathrm{mol}^{-1} \qquad ($	(1)
$\rm CO_2 + H_2 \leftrightarrow \rm CO + H_2O$	$\Delta H^\circ = +41.2 \mathrm{kJ} \mathrm{mol}^{-1}$	(2)
$\rm CO + 3H_2 \leftrightarrow CH_4 + H_2O$	$\Delta H^{\circ} = -228 \mathrm{kJ} \mathrm{mol}^{-1} \qquad ($	3)
$CH_3OH + H_2 \leftrightarrow CH_4 + H_2O$	$\Delta H^{\circ} = -159.4 \text{ kJ mol}^{-1}$	(4)

As can be observed in Figure 8a, the relatively low CO₂ conversion of 0.24– 0.71% was presented over ZrO₂ at the reaction temperature range of 320–400 °C, implying that the presence of ZrO₂ alone was not sufficient to catalyze the CO₂ hydrogenation reaction. This result could be related with the surface adsorption properties of the ZrO₂ characterized by TPD. Although CO₂ could adsorb and desorb from the surface of ZrO₂ on the whole reaction temperature range (320–400 °C) (Figure 7), it was unable to react with H₂ owning to too strong adsorption of H₂ (Figure 6). For pure In₂O₃, CO₂ conversion increased from 6.7% to 29.04% upon increasing reaction temperatures from 320 to 400 °C, which were significantly higher than those of ZrO₂. Obviously, nearly the same CO₂ conversion was acquired for all In₂O₃-ZrO₂ catalysts prepared with different calcination temperatures of ZrO₂ support when compared at identical reaction temperature and their CO₂ conversion was found to be the same level with the sole In₂O₃ at 320 °C. However, the lower CO₂ conversion was observed at a higher temperature of 340 °C and more pronounced at elevated reaction temperatures (360–400 °C).



Figure 8 CO₂ conversion and yield of CO, CH3OH and CH4 as a function of reaction temperature over In₂O₃, ZrO₂ and In₂O₃/ZrO₂ catalysts.

The yield of CO as a function of the reaction temperatures over the different catalysts are depicted in Figure 8b. The significant difference in CO yield could be observed between the ZrO₂ and In₂O₃ catalyst at identical reaction temperature. The ZrO₂ possessed evidently lower CO yield of 0.23–0.71% than that from the In₂O₃ catalyst (4.65–28.83%) at all reaction temperatures. Whereas, supporting In₂O₃ on ZrO₂ resulted

in an increase of CO yield compared to ZrO₂, but still lower than that for In₂O₃ catalyst. Increasing reaction temperature did not have a noticeable affect the formation of CO over ZrO₂, however, it was more favorable for In₂O₃ and In₂O₃-ZrO₂ catalysts. The CO yield of In₂O₃-based catalysts (In₂O₃ and 20In/Zr-X) showed an increasing trend with the increase of reaction temperature, which was due to the strong activation energy of RWGS reaction [27,29]. There was no significant difference in CO yield at each reaction temperature for the In₂O₃-ZrO₂ catalysts prepared with different calcination temperatures of ZrO₂ support. As well known, the RWGS reaction could proceed via a surface redox cycling mechanism in which metallic In was considered as an active site for the dissociative adsorption of CO₂, yielding an oxidic surface (In-O) and releasing CO (reaction (5)). Meanwhile, the reaction between the oxidic surface (In-O) with H₂ could produce metallic In surface back with H₂O product (reaction (6)). Accordingly, the catalyst with the highest metallic In content should have more ability to reduce CO₂ into CO. However, the CO yield was not correlated with the amounts of metallic In quantitatively determined by the linear combination analysis from TR-XANES results under reducing condition, which decreased in the following order: 20In/Zr-600> 20In/Zr-700> 20In/Zr-800> 20In/Zr-900> 20In/Zr-1000. A possible explanation stems from the fact that i) the RWGS reaction proceed via another mechanism, i.e. formate decomposition in which the metallic In is not the active site. ii) The In content of all catalysts after the reduction was not much different because the total content of In is only 20 wt%.

$$CO_2 + In \leftrightarrow CO + In - O$$
 (5)
 $In - O + H_2 \leftrightarrow H_2O + In$ (6)

Also in terms of CH₃OH productivity, ZrO₂ appeared to be almost inactive for CH₃OH synthesis, exhibiting CH₃OH yield close to 0 % at all reaction temperatures

(Figure 8c). Whereas In₂O₃ catalyst favored the formation of CH₃OH, the CH₃OH yields of In₂O₃ catalyst was found to be 1.97%, 1.12%, 0.58%, 0.28% and 0.14% at 320, 340, 360, 380 and 400 °C, respectively which were changed in the opposite manner to CO yield. In general, increasing temperature facilitated the CO₂ activation; however, the production of CO was favored rather than methanol due to the endothermic character. The similar trend of decreasing CH₃OH yield with the increase of reaction temperature was found for all In₂O₃-ZrO₂ catalysts. However, an improvement of CH₃OH yield on the whole temperature range over In₂O₃-ZrO₂ catalysts (except that of 20In/Zr-600 at 320 °C) was observed. By optimizing the calcination temperature of ZrO₂ supports, the highest yield of CH₃OH (2.51%) was achieved for the 20In/Zr-800 catalyst at 320 °C. However, at elevated reaction temperature (>340 °C), the ZrO₂ supports calcined at higher temperatures (20In/Zr-900 and 20In/Zr-1000) offered higher yields of CH₃OH compared to the 20In/Zr-800 catalyst. Based on the TPD results in Figures 6 and 7, the In₂O₃-ZrO₂ catalysts prepared at high calcination temperature (900 °C), characterized by rather strong interaction between catalyst surface and adsorbed species (CO₂ and H₂), exhibited a specific CH₃OH formation activity at elevated reaction temperature higher than the corresponding activity of the catalysts calcined at lower temperatures (600–800 °C). For example, at 360 °C, 380 °C and 400 °C, 1.57%, 1.19% and 0.85% CH₃OH yield were achieved over 20In/Zr-900, respectively. While the ZrO₂ supports calcined at lower temperatures reached 1.44%, 0.98% and 0.78% CH₃OH yield (20In/Zr-800), and 1.27%, 0.89% and 0.77% CH₃OH yield (20In/Zr-700), respectively, demonstrating that the calcination temperature emerged as a key parameter in yielding higher catalytic performance by tuning the strength of adsorbed CO₂ and H₂ with the catalyst surfaces. Nevertheless, the lower yields of CH₃OH (1.39%, 1.13% and 0.77%) were achieved over the 20In/Zr-1000 compared to 20In/Zr-900 catalyst (1.57%, 1.19% and 0.85%) at 360 °C,

380 °C and 400 °C, respectively. Attending to the aforementioned results, it could be concluded that calcination temperature of 900 °C was adequate for preparation of ZrO₂ to had sufficient surface adsorption strength in effectiveness for CO₂ hydrogenation to CH₃OH under elevated reaction temperatures (> 340 °C). Above this calcination temperature (1000 °C), the surface adsorption strength between H₂ and catalyst surface was improved even more, which could predictably dwindle the activity of the catalyst by suppressing the hydrogenation ability of the catalyst.

The yield of CH₄ over all catalysts at different reaction temperatures is presented in Figure 8d. The CH₄ yields obtained using ZrO₂ were close to 0.003% for all reaction temperature. Whereas, In₂O₃ catalyst provided the higher CH₄ yield of 0.06%. The CH4 yield of the In₂O₃ supported on ZrO₂ calcined at different temperatures were in the range 0.09–0.9%, slightly higher than both In_2O_3 (0.06%) and ZrO_2 (0.003%) at each reaction temperature. As illustrated in this figure, the 20In/Zr-600 catalyst exhibited the highest CH₄ yield of 0.64–0.9% under temperature variation. Furthermore, CH₄ yield showed a volcano profile with increasing reaction temperature and reached the highest value of 0.9% at 360 °C. Increasing calcination temperature of ZrO₂ support from 600 to 1000°C led to a decrease in CH₄ yield at each reaction temperature. The trendlines for the catalysts calcined at higher temperature (700-1000 °C) were similar to that presented for the catalyst prepared at low calcination temperature (600 °C). It is generally wellaccepted that the CO methanation (reaction (3)) and the hydrogenolysis of CH₃OH to CH₄ (reaction (4)) were involved for the production of CH₄. In present manuscript, we cannot conclude that which mechanism dominates the CH₄ formation. However, both mechanisms require the surface active H atom which has a weak interaction with the catalyst surface. Based on the H2-TPD analysis (Figure 6), the 20In/Zr-600 showed a higher amount of H₂ desorption at temperature ranging from 300-400 °C compared to

other catalysts, affirming the larger fraction of surface active H facilitating the formation of CH₄ from both hydrogenation of CO and hydrogenolysis of CH₃OH.

Figure 9 shows the CH₃OH yields over 20In/Zr-900 and 20In/Zr-1000 catalysts as a function of time-on-stream. The 20In/Zr-900 and 20In/Zr-1000 catalysts exhibited the maximum CH₃OH yield of 1.57% and 1.42% at 2 h and 1 h time-on-stream experiment which then slightly reduced to 1.51% and 1.34% at 50 h time-on-stream experiment, respectively. TEM images (Figure 10) of 20In/Zr-900 and 20In/Zr-1000 catalysts before and after activity test revealed that the nanostructures of both catalysts after reaction (50 h) were similar to those before reaction, suggesting a high stability of 20In/Zr-900 and 20In/



Figure 9 CH₃OH yield as a function of time-on-stream over 20In/Zr-900 and 20In/Zr-1000 catalysts. Reactions was performed at 360 °C, 20 bar and 75 mL min⁻¹ of CO₂/H₂/N₂ stoichiometric ratio of 1:3:1.



Figure 10 TEM images of 20In/Zr-900 before (a) and after (b) reaction and 20In/Zr-1000 before (c) and after (d) reaction.

4. Conclusions

A series of In_2O_3/ZrO_2 catalysts were prepared with different calcination temperatures of ZrO_2 support for CO_2 hydrogenation to methanol at high reaction temperatures (320–400 °C). By altering the calcination temperatures of ZrO_2 support, physicochemical properties, including phase, crystallinity, BET surface area, CO_2 and H_2 adsorption-desorption behaviors of In_2O_3/ZrO_2 catalysts could be modified. It was

concluded that the adsorption strength of reactants with the catalysts surface predominantly controlled the formation of CH₃OH. The weak adsorption strength (20In/Zr-600) facilitated the formation of CH₄. The stronger adsorption strength (20In/Zr-700, 20In/Zr-800 and 20In/Zr-900) enhanced the CH₃OH formation at elevated reaction temperatures. However, too strong adsorption strength of 20In/Zr-1000 decreased the yield of CH₃OH. The highest CH₃OH yield was achieved for 20In/Zr-800 and 20/In-Zr-900 at reaction temperatures of 320–340 °C and 360–400 °C, respectively.

Credit author statement

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Thongthai Witoon: Conceptualization, Methodology, Writing- Reviewing and Editing.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1 Textural properties of the In_2O_3/ZrO_2 catalysts prepared with different calcination temperature of ZrO_2 support.

Catalysts	BET surface area (m ² g ⁻¹)	Total pore volume	Average pore
		(cm ³ g ⁻¹)	size
			(nm)
20In/Zr-600	159	0.20	5.1
20In/Zr-700	119	0.15	5.1
20In/Zr-800	110	0.15	5.2
20In/Zr-900	91	0.13	5.8
20In/Zr-1000	51	0.09	7.3