Optimizing Pd:Zn molar Ratio in PdZn/CeO₂ for CO₂ Hydrogenation to Methanol

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Graphical Abstract

Highlights

- 14% CO₂ conversion and 95% methanol selectivity were achieved over PdZn/CeO₂
- 1.0PdZn/CeO₂ catalysts showed optimum catalytic performance
- Two possible routes for methanol formation *via* formaldehyde and/or formic acid hydrogenation are proposed.

Abstract

We report the compositional optimization of Pd:Zn/CeO₂ catalysts prepared *via* sol-gel chelation for the hydrogenation of CO₂ under mild reaction conditions. The formation of a PdZn alloy, which is the main active phase for this reaction, was maximized for catalysts with a Pd to Zn ratio close to 1. For these catalysts, a maximum conversion of 14%, close to thermodynamic equilibrium, and high selectivity to methanol (95%) were achieved at 220 °C, 20 bar, 2400 h⁻¹ GHSV and H₂:CO₂ stoichiometric ratio of 3:1. The formation of PdZn alloys was achieved by reducing the catalyst precursor at 550°C under hydrogen flow and confirmed by XRD. XPS confirmed the presence of Pd⁰, being maximum for the optimized catalyst composition. Two competing reactions were observed over the catalysts, methanol synthesis and RWGS reaction. RWGS reaction is responsible for the production of CO and its selectivity increases with temperature. At lower temperature, i.e. 180 °C, 1.0PdZn catalyst showed 100% selectivity to methanol at 8% CO₂ conversion. In good agreement with the literature, at higher space velocities, the selectivity to CO decreases. *In situ* DRIFTS suggests that CO₂ is activated as CO₃⁻ over CeO₂. Surface micro-kinetics demonstrates that methanol can be formed either *via* formaldehyde or formic acid surface intermediates.

Keywords: PdZn alloy, CeO₂, Citric acid, Chelating agent, Methanol synthesis, DRIFTS.

1. Introduction

Global energy demand is estimated to reach about 20 billion tonnes of oil equivalent (BTOE) by 2040 [1], from which approximately a 70% will be derived from fossil fuels, consequently increasing atmospheric carbon build-up. To objectify the target of limiting the average global temperature rise below 2°C, most countries of the world have agreed to cut down their CO₂ production [2]. In this spirit, Olah [3] proposed the “methanol economy”, whereby atmospheric CO₂ (0.041%) and those captured from industrial effluents can be converted to methanol, a convenient liquid fuel, hydrogen storage material and feedstock for hydrocarbon syntheses and their products. To make this process carbon neutral, the required hydrogen must be supplied from renewable sources, i.e. hydrogen *via* water splitting using energy sources like solar, wind or hydrothermal [4].

Currently methanol is produced using syngas over a Cu/ZnO/Al₂O₃ catalyst at 250-300°C and 50-100bar [5, 6]. Unfortunately, the use of similar Cu-based catalyst for the hydrogenation of CO₂ requires excessive pressures to reach decent selectivity to methanol [7,8].

These challenges have opened research opportunities in the search for alternative catalysts for CO₂ hydrogenation to methanol. Pd-based catalysts have proven to be resistive to sintering and more stable than the conventional Cu-based catalysts for this process, although they suffer from low activity at low temperature and low selectivity at high temperature [9,10]. The formation of bimetallic alloys (PdZn, Pd-Ga, PdZr) of Pd-supported on ZnO, Ga₂O₃ and ZrO₂ showed enhanced catalytic activity and selectivity to methanol compared to Pd/support alone [11-18]. Bahruji et al. studied the influence of PdZn particle size over CO₂ conversion and methanol selectivity [14,19] and found that smaller particles, with a strong interaction with the support, result in more selective catalysts. Pd/Zr catalysts prepared *via* in-situ activation revealed isolation of Pd particles from the bulk and showed higher methanol yields than catalysts prepared by impregnation [20]. Xu et al. [9] investigated different preparation methods of PdZn

over Al_2O_3 and reported that co-precipitation method is superior over deposition precipitation and impregnation methods in terms of methanol selectivity.

Supports like ZrO_2 , ZnO , SBA-15, MCM-48, Ga_2O_3 and CeO_2 have been tested as potential supports for Pd in CO_2 hydrogenation to methanol [9, 16, 20, 21]. However, CeO_2 promotes CO_2 activation at the metal/support interface due to its ability to create surface and bulk oxygen vacancies [22]. Doping Ca on PdZn/ CeO_2 catalysts improved surface basicity and subsequently assisted the reducibility of ceria by creating more oxygen vacant sites and enhanced catalytic activity [13]. Pd promotion in Cu/ CeO_2 based catalysts improves the dispersion of Cu and overall catalytic activity [23,24]. High cost of Pd (\$40.58/gram) leads to necessary of its loading optimization in catalysts.

Our group recently reported PdZn/ CeO_2 (5wt% Pd) catalysts for CO_2 hydrogenation to methanol *via* sol-gel technique, where structural and textural properties of the catalyst can be controlled using this preparation method [25], showing enhanced activity and selectivity for this process [13]. This research focuses on optimizing Pd:Zn molar ratio over CeO_2 support prepared *via* citric acid (CA) chelation method. The synthesized catalysts were characterized using BET, XRD, XPS, SEM/EDX, EELS-STEM, CO_2 TPD, H_2 -TPR techniques to determine physiochemical properties and to correlate intrinsic catalytic performance and surface properties. *In situ* DRIFT studies were performed in an attempt to identify the surface reaction mechanism for methanol synthesis.

2. Experiment

2.1. Catalyst Preparation Procedure

PdZn/ CeO_2 catalysts with varying Pd:Zn nominal molar ratio (0.7 to 1.1) were synthesized *via* sol-gel using CA as chelating agent as reported in our previous report (CA:Metal molar ratio

of 3:1) [13]. Throughout this article, the prepared catalysts are named as 0.7PdZn, 0.9PdZn, 1.0PdZn and 1.1PdZn, where the preceding number designates the corresponding molar ratio. The weight percentage of Zn was kept constant (5wt%) while varying Pd loading to attain the desired Pd:Zn molar ratio. Briefly, a calculated amount of nitrate salts (Pd, Zn and Ce) and CA were dissolved in 30ml water contained in separate beakers and mixed dropwise; $\text{Pd}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ to $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ salt to CA. Obtained Pd-Zn and Ce-CA solutions were mixed under stirring at 90°C . As the interaction approached end-point, the metal ions began to form a suspension in CA which finally was evaporated leaving behind a gel of integrated network. The gel was aged for 24hrs at 90°C in a water bath followed by overnight drying in an oven at 110°C . The dried catalyst was pulverized and calcined in dry air in an open crucible at a temperature of 500°C for 5hrs ($5^\circ\text{C}/\text{min}$ ramping rate) leaving behind the oxidic form of catalytic precursors.

2.2. Characterization Methods

N_2 -physiosorption analysis was conducted at 77K using a Micrometrics NOVA 2200e analyzer. Catalyst samples were degassed at 300°C for 2hrs prior to analysis to remove entrapped moisture. The surface area, pore volume (PV) and pore size distribution (PSD) were obtained utilizing Brunauer-Emmett-Teller (BET) at a relative pressure range of $P/P^0 = 0.05$ -0.3 and non-local density functional theory (NLDFT) equilibrium models of slit pore geometry. Pore volume were estimated from N_2 isotherms at a relative pressure of $P/P^0 = 0.98$ by utilizing the bulk liquid N_2 density.

Temperature programmed reduction (H_2 -TPR) analysis of calcined catalysts was conducted using a Quantachrome Pulsar Analyzer. Typically, 0.1g of a sample was loaded into a U-type quartz reactor and adsorbed moisture was removed from the surface of the catalyst at 150°C

under Ar flow for about 2h and the temperature was then cooled down to 30°C. TPR experiments were conducted from room temperature to 800°C under 20ml/min flow of 5% H₂/N₂ mixture at a ramping rate of 10K/min, during which the H₂ consumption was recorded.

Temperature programmed desorption (CO₂-TPD) analysis of all calcined samples was carried out using a micromeritics (AutoChem HP) chemisorption analyzer coupled with a mass spectrometer. Similarly to TPR experiments, 0.1g of a sample was loaded into a u-type reactor. Prior to CO₂ adsorption, catalyst precursors were reduced at 550°C under H₂ flow (20 mL/min) for 1 h and then cooled down to room temperature under 20 mL/min He flow for 2 h. Then, the in situ reduced catalyst was saturated with a 20 mL/min flow of 15% CO₂/Ar mixture for 1h followed by TPD experiment with a heating rate of 10°C/min under He flow (50 mL/min).

X-ray Diffraction (XRD) analyses were carried out at room temperature in the diffraction angle range of 0-110° using an Equinox 1000 diffractometer (Co-K α radiation of 0.1709 nm wavelength).

X-ray photoelectron spectroscopy (XPS) was performed on a SPECS GmbH (Germany) with non-monochromatic Al-K α X-ray radiation (1486.6 eV). In a typical analysis, the sample was stuck to a double-sided carbon adhesive tape and attached to the sample holder. Then, the sample was introduced into the load lock chamber and evacuated overnight until ultra-high vacuum (UHV) pressure of 10⁻⁸ mbar was reached. This is followed by transferring the sample into the analysis chamber under UHV pressure of 4.8 x 10⁻¹⁰ mbar for analysis. XPS data were acquired utilizing a PHOIBOS 150 MCD-9 hemispherical energy analyzer. Adventitious carbon (C1s) at 284.8 eV corresponding to graphite was used as binding energy (B.E) reference for charge correction [26]. The deconvolution of the XPS peaks and the evaluation of the spectra were performed using the CasaXPS software package version 2.3.16.

Energy dispersive spectroscopy (EDS) with a scanning electron microscope (SEM) was performed on a Quanta FEG 450 (FEI Brand) to determine the elemental composition and its distribution over catalysts grain.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted using a Bruker Tensor II FTIR spectrometer installed with Harrick praying mantis and ZnSe window. All experimental infrared spectra were recorded in the wavenumber range of 800-4000 cm^{-1} . In the standard procedure, about 0.1g of catalyst was loaded into the sample holder and the catalyst was reduced for 1hr under 20ml/min H_2 flow at 550°C (atmospheric pressure) and subsequently cooled to desired reaction temperature (220°C). At this temperature, the catalyst was exposed to 15ml/min Ar flushing for about 2hrs to remove gaseous and weakly adsorbed species before taking the background spectrum. Then, the catalytic experiments were performed under 20ml/min CO_2/H_2 mixture (or CO_2) flow to determine the intermediate species formed at different reaction conditions (temperature and pressure). Spectra were obtained continuously by averaging 100 scans with 4 cm^{-1} resolution and 30 IR spectra and were collected at 2mins interval for 1hr.

2.3. Methanol Synthesis Reactor Setup

Catalyst activity was tested in a tubular fixed-bed micro reactor (9.1mm x 300mm), equipped with Bronkhorst mass flow controllers and temperature sensors. In a typical experiment, the reactor was packed with 0.05g of quartz wool and 0.5g of calcined catalyst. The catalyst was exposed to 20ml/min Ar flow while the temperature was raised to 550°C. At this temperature, the flow was switched to 20ml/min H₂ for 1hr to reduce the catalyst and then subsequently cooled down to the desired reaction temperature (i.e. 220°C). Afterwards, 20ml/min flow of CO₂/H₂ with stoichiometric feed ratio of 1:3 was fed into the reactor and pressure was raised to 20bar (1bar/min ramp). Methanol synthesis reaction was conducted until steady state was achieved (3hrs unless otherwise stated). Online product stream analyses were performed using gas chromatography (GC) (Agilent 7890B) equipped with HP-pona capillary column for FID (methanol detection) and Haysep Q-packed column for TCD (H₂, CO and CO₂ detection). To avoid product condensation, the post reaction line was maintained at a temperature of 150°C for all experiments. Product analysis was performed by taking an average of three independent readings (within the reproducibility range of 5% error) and the data reported herein for product selectivity, methanol space-time yield (STY) and CO₂ conversion were calculated using Eqs. (1-3).

$$\text{CO}_2 \text{ Conversion: } X_{\text{CO}_2}(\%) = \frac{F_{\text{CO}_2\text{in}} - F_{\text{CO}_2\text{out}}}{F_{\text{CO}_2\text{in}}} * 100 \quad (1)$$

$$\text{Methanol Selectivity: } S_{\text{MeOH}}(\%) = \frac{F_{\text{MeOH}}}{F_{\text{CO}_2\text{in}} - F_{\text{CO}_2\text{out}}} * 100 \quad (2)$$

$$\text{Methanol STY: } \text{STY}_{\text{MeOH}} = \frac{\text{Mass of MeOH (g)}}{\text{Catalyst weight (g)} \times \text{Hour}} \quad (3)$$

F_i = Molar flow rate of species 'i'.

3. Results and Discussion

3.1. Catalysts Characterization

3.1.1. Surface Area and Pore Size Distribution

The textural properties of calcined and reduced (fresh) catalysts were measured by performing N₂ physisorption analysis at 77 K. The adsorption isotherms of all reduced catalysts (Fig. 1A) are typical of type IV. The existence of a hysteresis closing at 0.42 P/P⁰ is a characteristic which indicates the presence of mesopores smaller than 3.4 nm and bigger cavities in the catalyst structure [27, 28]. BET surface area of the reduced catalysts was determined in the range of 36-43 m²/g (Table 1). The pore volume of the fresh catalysts increased with increasing PdZn molar ratio from 0.05-0.09 cm³/g when PdZn ratio was increased from 0.7 to 1.0 and then observed a decrease in PV (0.05 cm³/g) for 1.1PdZn catalyst (Table 1). This can be attributed to the formation of larger pores during chelatization. Such an increase in pore volume is more evident in the PSD plot shown in Fig. (1B) with a broad peak at 4.2 nm in the mesopore region. For 0.7, 0.9 and 1.1 PdZn catalysts, two families of pores confirm the presence of a micro and mesopore bimodal structure. However, the 1.0PdZn catalyst contains only a mesoporous structure in the range of 4-15 nm.

3.1.2. CO₂- TPD

TPD analysis of adsorbed CO₂ was conducted in He flow to understand the basicity of the *in situ* reduced catalysts (Fig. 2A). All the spectra exhibited low CO₂ desorption temperature with peaks in the range of 80-91°C, attributable to CO₂ physically adsorbed on the catalyst surface. Fan and Fujimoto [29] reported the possibility of CO₂ to decompose into CO over Pd/CeO₂ at low temperature. The amount of CO₂ desorbed from the catalyst surface for all samples ranged from 51-75 μmol/g_{cat} (Table 1). The 1.0PdZn catalyst showed the highest amount of desorbed CO₂ (75 μmol/g_{cat}). Our group previously reported that the presence of PdZn alloy notably

modified the basicity of ceria [13]. CO₂ peak around 90°C is attributed to the decomposition of b-HCO₃⁻ while the shoulder peak around 210°C indicates b-CO₃²⁻ and m-CO₃²⁻ species [30]. As the catalysts were reduced *in situ* using hydrogen, H₂ is desorbed at 55-75 °C (*vide infra*) and is responsible for the formation of HCO₃⁻.

3.1.3. H₂ – TPR

The reducibility of the different catalysts was studied using H₂-TPR (Fig.2B). A negative peak, which corresponds to the decomposition of palladium hydride (PdH_x) was observed at the temperature range of 55-75°C over all the catalysts [13,19]. PdH_x is unstable and usually decomposes during high temperature reduction, releasing hydrogen and subsequently producing a negative peak [31]. A narrow peak observed at 70-110°C and additionally, another peak at 150-220°C can be attributed to the reduction of PdO species over the surface, which may arise due to the strong interaction of small Pd particles with CeO₂ support [32].

A slight shift of reduction peak centered around 300°C can be attributed to the reduction of ZnO. The incorporation of Pd in Zn structure is responsible for the early reduction of Zn which otherwise is reported to start at 400°C [33]. The reduction of surface oxygen of ceria occurs at about 400-600°C while bulk ceria reduction only occurs at approximately 800°C [13, 34]. Nevertheless, similar reduction peaks which are attributable to the partial reduction of surface CeO₂ are observed at 350-500°C for all the samples and are in agreement with previous reports by Zhu et al. [35]. It can be deduced from the TPR spectra that the presence of Pd and Zn assists in decreasing the surface CeO₂ reduction temperature. In addition, the TPR profile shows a significant release of hydrogen (negative peaks) over all the catalysts at approximately 700°C probably indicating the spillage of H₂ from Pd to CeO₂ and its release from the surface.

3.1.4. XRD

The crystallographic structure of calcined and freshly reduced catalysts was analyzed using XRD (Fig. 3A, B). Hexagonal ZnO (101) phase observed at a diffraction angle of 42.4° in calcined catalysts is ascribed to thermal decomposition of zinc nitrate during the calcination step. However, no diffraction peak of PdO in the calcined catalyst was observed, suggesting a very small crystallite size or the formation of amorphous oxide phases. The presence of a small peak attributed to Pd₂Zn (110) was observed at 49° (specially for 1.1PdZn) [15]. Freshly reduced catalysts revealed two distinct diffraction peaks at 48° (111) and 51.7° (200) respectively, corresponding to the formation of β -PdZn tetragonal crystal phase. These diffraction peaks appeared at about 42° and 44° respectively when Cu-K α radiation ($\lambda = 0.0154\text{nm}$) was used in previous reports [11,14,36].

Scherrer's equation was employed (supplementary information SI-1) to estimate the crystallite size of different phases observed during XRD analysis and are shown in the supplementary information (SI). The crystallite size of cubic CeO₂ (111) phase for freshly reduced catalysts is in the range of 9.8-10.1nm and increases with the increasing PdZn loading, in good agreement with the textural characterization. Crystallite size of β -PdZn (111) and (200) phases are in the range of 14.3-15.2nm and 11.5-14.4nm respectively (Table 1).

3.1.4. XPS

The XPS analysis of freshly reduced catalysts reveals the surface oxidation states of Pd, Zn, Ce and O species. Fig. (4) displays the XPS spectra of Pd (3d_{5/2}) in the range of 335.5-335.9. Deconvolution of these B.E. peaks shows that Pd is present as Pd⁰, Pd²⁺ and Pd⁴⁺ oxidation states (Table 2) in accordance with other reports [13, 26, 37, 38]. The positive B.E. shift of 0.4-0.8eV observed for Pd⁰ oxidation state (in this work) can be ascribed to the presence of PdZn alloy on the catalyst surface [39]. This finding is supported by the identification of PdZn

crystal phase over CeO₂ according to XRD analysis. The B.E. peak intensities of Pd⁰ (in form of PdZn), shown in Table (2), increases with increasing Pd:Zn molar ratio, probably due to the of disruption of Pd and Zn interaction on exposure to air [38] . We estimated the relative amount of surface Pd⁰ present on the catalysts to vary from 83- 85mol% with 1.0PdZn showing the highest concentration of Pd⁰ species (Table 2). High concentration of surface Pd⁰ in the 1.0PdZn catalyst may be responsible for the best catalytic performance which is explained in the activity section.

No peak was observed at B.E. 992 and 996eV, typical of metallic Zn [40]. Meanwhile, core level Zn 2p_{3/2} peak at 1022eV was identified (Supplementary Fig. SF1). Zn LMM Auger analysis was employed to investigate the change in the chemical state of Zn since a significant B.E. shift relative to Zn metal was expected (Supplementary Fig. SF2). The presence of Zn Auger peak at 998eV revealed that most of the Zn present in the catalysts exist as Zn²⁺ most probably as ZnO, indicating surface Zn is oxidized with the exposure in air and a peak/shoulder at 991eV may attribute for interstitial Zn on the catalyst surface [19, 41-43]. XPS spectra of O 1s for all catalysts revealed that main B.E. peak was at 529.0-529.5eV, corresponding to oxygen bonding to cerium and a positive B.E. shift was observed with increasing Pd:Zn molar ratio. Also, a shoulder peak at 531.5eV was deconvoluted into peaks indicating the presence of adsorbed hydroxyl and water on the catalyst surface respectively, which comes mainly from the atmosphere (Supplementary Fig. SF3 and SF4).

The main Ce (3d_{5/2}) B.E. peak identified in the range of 882.6-883.3eV, corresponds to Ce⁴⁺ (v doublet) and agrees with Matsumura et al. [26, 34]. The B.E. of Ce (3d_{5/2}) and (3d_{3/2}) energy levels for all catalysts revealed satellite pairs of u^{''}, u^{''}, u, v^{'''}, v^{''} and v peaks with shake-up and shake down characteristics in agreement with Bêche et al. [26,44] and are shown in Fig. 5. Pairs of Ce³⁺ doublets (v^o, u^o, u['] and v[']) observed during XPS analysis confirms the occurrence of partial reduction of ceria (Supplementary Fig. SF5 and Table 3).

3.1.5. EDS/SEM and STEM-EELS Analysis

EDS coupled with SEM was used to quantify the elemental analysis and distribution of species in the catalysts and the mappings/spectra are shown in Fig. 6 and in supplementary Fig. (SF6-SF8). The nominal weight percentages of Pd and Zn used for catalyst preparations closely agreed with EDX elemental quantification (Supplementary Table ST1). The triangular phase-diagram for 1.0PdZn shown in Fig. 6 reveals the formation of Pd and Zn elements over ceria in a heterogeneous (non-uniform) distribution but Pd and Zn elements are in close proximity (Pd-Zn region), suggests the formation of PdZn alloy over CeO₂.

The catalyst with Pd:Zn ratio of 1:1 was also studied using a transmission electron microscope FEI's Titan ST 300kV operated in STEM mode. Electron energy loss spectroscopy (EELS) was used for elemental mapping of the sample. For EELS data treatment, Gatan Digital Micrograph v.3.30.2016.0 was used. Elemental maps for the 1.0PdZn catalyst is shown in Fig. 7. From the figure, we can see the proximity of Pd and Zn which may be caused by the Pd-Zn alloy formation. Also, high carbon contamination which is observed from microscopy data can be related to the remaining citric acid from the precursor solution.

Supplementary Fig. SF5- SF6 (d) display the mapping and phase diagram of other catalysts, confirming the non-uniform distribution of Pd and Zn species on the CeO₂ support. However, we observed the additional presence of Zn nanoparticles (for 0.7 and 0.9 PdZn catalyst) beyond the Pd-Zn region which indicates the presence of ZnO and agrees with Matin [45]. Similar ZnO was also observed in XRD and XPS analyses, which may be a cause of air oxidation of Zn.

3.2. Catalytic Activity Performance

3.2.1. Influence of reaction temperature

The influence of temperature in the range of 220-270°C (keeping the pressure at 20 bar and GHSV at 2400h⁻¹) on catalytic performance of the prepared catalysts for CO₂ hydrogenation to methanol was investigated and results are depicted in Fig. 8A. All the catalysts showed a rapid increase in CO₂ conversion until 250°C after that increase in conversion was slowed down, except for 1.0PdZn catalyst for which CO₂ conversion is higher compared to other samples, showing a linear increment of activity with temperature. CO₂ conversion over 0.7, 0.9 and 1.1PdZn catalysts are almost the same at 250°C (14%) and 270°C (15%), suggesting that the reaction is operating close to thermodynamic equilibrium at these conditions. Methanol selectivity was observed to decrease with increasing the reaction temperature due to RWGS (Fig. 8B). These observations are convened in a methanol selectivity – CO₂ conversion curve (Fig. 8C), which clearly shows that with the increase in reaction temperature, methanol selectivity decreases with increasing CO₂ conversion for all the tested catalysts. In summary, 220°C is the best temperature to operate and 1.0PdZn catalyst showed a CO₂ conversion of 14% and maximum methanol STY of 114g/kg_{cat}/hr with a methanol selectivity of approximately 95% revealing a superior performance over other catalysts reported for this reaction at similar reaction conditions (Table 4). The performance of the best catalyst (1.0PdZn) was also investigated at low temperature and interestingly showed 12% CO₂ conversion and 98% selectivity at 200°C and 8% CO₂ conversion and 100% methanol selectivity at 180°C.

3.2.2. Influence of Pd:Zn Molar Ratio

Fig. 9A shows the influence of Pd:Zn molar ratio on catalytic activity at 220 °C, 20 bar and 2400 h⁻¹ GHSV. Methanol selectivity (Fig. 9B) was decreased with increasing Pd:Zn molar

ratio while selectivity to CO expectedly increased which suggests that increasing amount of Pd loading enhances the RWGS reaction.

A significant enhancement in CO₂ conversion and methanol space time yield (STY) were observed as the Pd:Zn ratio is increased from 0.7 to 1.0 reaching a maximum for 1.0PdZn. Further increase in Pd:Zn ratio revealed a notable drop in catalytic activity. Remarkably, optimum STY of methanol over 1.0PdZn catalyst showed about 58% higher than 1.1PdZn catalyst corresponding to 114 and 72g/kg_{cat}/h respectively. Table (4) reports the activity results of the investigated catalysts and compared other PdZn based catalysts reported in the literature. Surface characterization of the catalysts revealed that the highest relative content of Pd⁰ species, present as PdZn bimetallic alloy (XRD, XPS section) in the 1.0PdZn catalyst, which is the optimum Pd:Zn ratio over CeO₂ surface for this hydrogenation reaction for methanol synthesis. From the XPS analysis shown in Fig. 10, the surface content of Pd⁰ (considered as PdZn alloy as discussed in XPS section) went through a maximum for 1.0PdZn catalyst which is also correlated with the best activity of CO₂ conversion and high methanol selectivity.

3.2.3. Stability of 1.0PdZn/CeO₂ Catalyst

Time-on-stream (TOS) experiment was conducted to test the stability of the best catalyst at the optimum reaction conditions (220°C, 20bar, 2400h⁻¹ GHSV) and shown in supplementary Fig. (SF9). Methanol selectivity reached steady state at approximately 3hrs and within the next 30hrs, some deactivation was observed (12.5% CO₂ conversion and 91.6g/kg_{cat}/h STY) and after that, the catalyst activity was stable for more than 100hrs. This showed approximately 20% decrease in STY compared to the initial activity. A close comparison of XRD for TOS spent (Fig. SF10) and fresh samples showed no formation of new phases except an insignificant reduction in the PdZn (111) intensity peak. The crystal growth of PdZn particles (14.3 to 15.2nm) as evidenced from XRD analysis, reduced catalytic activity (sintering) during a long exposure in reaction condition. Also, the susceptibility of PdZn catalyst for water formation

via RWGS is well known [46] and might significantly contribute to the deactivation through sintering. As the activity reached equilibrium after 30hrs (Fig. S9), the attained CO₂ conversion and methanol selectivity was quite high compared to Cu-based catalyst at this mild operating condition, which brings in to the conclusion that Pd-based catalyst can be a potential alternative catalyst for CO₂ hydrogenation to methanol.

3.2.4. Effect of Gas Hourly Space Velocity (GHSV)

Catalytic performance of the best catalyst was tested by varying GHSV from 2,400-12,000 h⁻¹ at the optimum operating condition of 220°C and 20bar. At maximum GHSV (12,000h⁻¹), the STY of methanol reached 304g/kg_{cat}/h with CO₂ conversion and methanol selectivity of 7.4 and 100% respectively (Fig. 11A). In addition, at long residence time (lowest GHSV of 2400h⁻¹), catalytic performance approaches thermodynamic limit revealing the highest CO₂ conversion of about 14% and lowest methanol STY of 114g/Kg_{cat}/h. Although, for commercial operation, GHSV lower than 2,400h⁻¹ may not be practically applicable from an economic standpoint since the methanol space time yield will be very low. Generally, as the GHSV increases, CO₂ conversion and CO selectivity decrease while methanol selectivity and STY increase. The decrease in CO₂ conversion can be attributed to a reduced amount of adsorbed CO₂ on the surface of the catalyst at low contact time (high GHSV).

3.2.5. Effect of Total Pressure

The influence of system pressure (1- 40bar) on the performance of 1.0PdZn catalyst were tested at the temperature and GHSV of 220°C and 2,400h⁻¹ respectively (Fig. 11B). It showed that as

pressure increases from 1-20bar, CO₂ conversion and methanol STY increased and reached a maximum at 20bar. At higher pressure above 20bar, a decrease in the activity was observed for the catalyst. This may be due to a high occupation of the surface with H₂ (with CO₂:H₂=1:3 feed) which may inhibit adsorption and reaction of CO₂ over the catalyst surface. At 1, 5, 10 and 15bar, we have a considerable amount of conversion with a very high selectivity to methanol. CO₂ conversion and methanol selectivity of 3% and 85% respectively with methanol STY (19.1g/kg_{cat}/h) at atmospheric pressure is superior to Iwasa et al. [11] who previously reported a methanol selectivity of 65% at 1bar over Pd/ZnO catalyst. The activity of this catalyst at atmospheric pressure suggests that it is feasible to synthesize high performing catalyst for low-pressure (1-5bar) CO₂ hydrogenation to methanol which can be further converted to lower olefins/dimethyl ether in a single pass reactor.

3.3. DRIFTS Study

3.3.1. Pure CO₂ adsorption on 1.0PdZn catalyst

Fig. 12 displays the FTIR spectra of pure CO₂ adsorbed over 1.0PdZn catalyst. The adsorption was carried out at a temperature range of 50-250°C and at constant atmospheric pressure. The wide band observed at 2361cm⁻¹ is assigned to gaseous CO₂ adsorbed on CeO₂ surface. Within infrared (IR) band of 1800-800cm⁻¹, about nine peaks were observed exhibiting different mode of CO₂ adsorption with increase of adsorption temperature. Strong bands at 1301-1310 and 1574 cm⁻¹ are typical of symmetric and asymmetric bidentate surface carbonate (b-CO₃²⁻) observed at temperatures of 50-100°C. These peaks disappeared with the increase of temperature and formed different adsorption modes having frequency at 1472-1480 and 1078cm⁻¹ attributable to monodentate surface carbonate species [47]. Also, IR bands observed at 1078 and 1175cm⁻¹ can be assigned to surface monodentate and bridged carbonates [47],

while bands at 1030-1040 and 1397 cm^{-1} are typical for surface hydrogen carbonates (HCO_3^-) which are probably formed by reacting adsorbed CO_2 with surface Ce-OH species. Surface monodentate carbonate species was formed at high temperature via the decomposition of HCO_3^- intermediates, as observed in CO_2 TPD study.

3.3.2. CO_2/H_2 adsorption on pure ceria support

The adsorption of CO_2/H_2 mixture on pure ceria support surface was also carried out at the optimal operating condition (220 $^\circ\text{C}$, 20bar) and results are depicted in two sections (Fig. S11). Within first 20 minutes of adsorption, hydrogenated species which are attributable to $\nu(\text{C-H})$ and $\delta(\text{C-H})$ of surface formates (HCOO) at 2848 and 2933 cm^{-1} respectively were observed [48]. These two bands got intensified with prolonged adsorption time. The band at 2177 which belong to adsorbed CO on reduced ceria (Ce^{3+}), was increased in concentration while linearly adsorbed CO_L at 2053 cm^{-1} vanished with increasing adsorption time probably to assist in the formation of other intermediate species. Bands at 1258 and 1354 cm^{-1} are attributed to $\nu_s(\text{OCO})$ and $\delta(\text{CH})$ vibrational mode of formate species. Shoulder at 1754 cm^{-1} is assigned to formaldehyde (H_2CO) while the wide band which was increasing with adsorption time around 1600 cm^{-1} has been reported for water [49]. Band range of 1023-1062 cm^{-1} is attributed to $\nu(\text{CO})$ stretching of methoxy species on ceria surface containing different coordination geometry [47]. However, we observed no $\nu(\text{C-H})$ vibrational mode of methoxy species on pure ceria support surface.

3.3.3. CO_2/H_2 adsorption over 1.0PdZn catalyst with temperature variation

The effect of temperature on CO_2/H_2 adsorption over 1.0PdZn was also studied. The temperature was varied in the range of 100-220 $^\circ\text{C}$ at 20 bar pressure and the spectra were

monitored for 1h and the final steady state spectra are depicted in Fig. 13. Three major peaks of intermediate species were identified at band range of X (2700-3000), Y (2000-2200) and Z (1000-1800) cm^{-1} respectively. At a low temperature of 100°C, there was no evidence of molecular adsorption of methanol as only weak peaks of linearly adsorbed CO were observed. This means that even at such a low temperature, the dissociative adsorption of CO_2 on the catalyst surface to form CO is possible. However, the available energy needed to activate the formation of surface intermediates for methanol was not enough. As the temperature was raised to 150°C, bands typical of methoxy species and gaseous methanol began to form and these bands grew large with increasing temperature in both X and Y ranges. At optimal reaction condition (220°C, 20bar), IR intensities of methanol and methoxy species were observed to vary more than five folds compared to the bands at 150°C.

Overlapping peak intensities at respective IR bands of 2821, 2867 and 2922 cm^{-1} belong to $\nu(\text{C-H})$ vibrational mode of methoxy species [47] while peaks at 2846 and 2970-2997 cm^{-1} are also traceable to methanol [49]. This $\nu(\text{C-H})$ mode of methoxy species was not observed during adsorption on pure ceria support indicating that this is a key intermediate for methanol formation and the presence of Pd assisted its formation via H-adspecies spillover to CeO_2 support and react with adsorbed CO_2 over CeO_2 surface. The peak at 2076 cm^{-1} is attributable to linearly adsorbed CO on PdZn alloy species which was formed after the reduction of catalyst surface in H_2 environment [14,50]. In the Z band range (1000-1800 cm^{-1}), $\nu(\text{CO})$ modes of methoxy species of different geometries were observed. IR bands at 1054 and 1023 cm^{-1} are assigned to type (II) bridged and type (III) triply bonded methoxy species present due to their thermal stability [48]. Peaks concentrated in the band range of 1300-1640 cm^{-1} for CO_2/H_2 adsorption are traceable to surface mono and bidentate formate species of different vibrational modes [49, 51]. IR bands attributable to molecularly adsorbed formic acid (HCOOH) were also observed at 1696-1684 and 1734 cm^{-1} respectively while the peak at 1752 cm^{-1} is typical of

formaldehyde (HCHO) species [48]. At 220°C, shortly after introducing CO₂/H₂ mixture onto the surface of the catalyst, IR peaks of methanol (2970 – 3000cm⁻¹) were observed and slowly increased with time. It suffices to assume that the presence of PdZn alloy accelerated the kinetics of methanol formation by lowering the activation energy for surface methoxy formation and this effect is a function of temperature.

3.3.4. CO₂/H₂ adsorption over 1.0PdZn catalyst – effect of pressure

Adsorption of CO₂/H₂ at varying pressure (1-20bar) and a constant temperature of 220°C was also carried out (Fig. SF12). We remarkably observed significant methanol formation rate at atmospheric pressure over the surface of 1.0PdZn catalyst. The capability of Pd based catalyst to convert CO₂ to methanol was also reported by Iwasa et al. [11]. In the pressure variation experiments, no new IR bands different from those discussed above were observed. Peak intensities $\nu(\text{C-H})$ stretching mode of methoxy species at 2923cm⁻¹ increased with increasing pressure which varies more than three folds when the result of 1 bar was compared to that of 20bar. The methanol peak intensities were also increased with increasing pressure. This effect was found to be more significant at 20bar compared to other tested pressure (1, 5, 10 bar). The peak intensity of methanol at 20bar doubles that of 5 and 10bar respectively while the difference between 5 and 10bar was not that obvious. Also, the increasing peak intensities of linearly adsorbed CO is an indication that dissociative adsorption of CO₂ is a direct function of pressure.

Conclusively, the formation of surface carbonate (CO₃⁻) species is the main step for activating CO₂ which occurs at the surface oxygen vacant sites of CeO₂, formed while reducing the catalyst at high temperature, forming surface Ce³⁺ species. Pd performs a dual role of activating and supplying hydrogen adspecies (H_s) necessary for hydrogenation and accelerating the kinetics of methanol formation. Observation of surface methoxy species, formaldehyde and

formic acid indicates two possible routes for methanol production, simultaneously happening over the surface. In the first route, hydrogenation of monodentate carbonate to formate occurs followed by subsequent hydrogenation to methanol via formaldehyde and methoxy intermediates while in the second route, formate is hydrogenated to methanol *via* formic acid and methoxy species intermediates.

4. Conclusion

The effect of Pd:Zn molar ratio (0.7 to 1.1) over CeO₂ support for CO₂ hydrogenation to methanol has been studied. Catalyst with a 1:1 Pd:Zn molar ratios showed the optimum performance under stoichiometric reaction conditions at 220 °C, 20 bar and 2400 h⁻¹ GHSV, with the reactant molar ratio 3:1 (H₂:CO₂), resulting in a methanol STY of 114g/kg_{cat}/h. Interestingly, this catalyst is also active under atmospheric conditions with 3% CO₂ conversion, 85% methanol selectivity and 19.1g/kg_{cat}/h methanol STY. In-depth *in situ* DRIFTS analysis suggests the surface mechanism for methanol formation *via* two competing surface reaction mechanism over this catalyst i.e. (1) hydrogenation of formate-formaldehyde-methoxy species (2) hydrogenation of formate-formic acid-methoxy species.

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Table 1 : Textural and desorption properties of freshly reduced catalysts.

Catalysts	N ₂ physiosorption			XRD crystalite size			CO ₂ TPD
	BET S/A (m ² /g)	P. Width (nm)	P. V (cm ³ /g)	PdZn(111) (nm)	PdZn(200) (nm)	CeO ₂ (111) (nm)	CO ₂ Desorbed (μmol/g _{cat})
0.7PdZn	42	3.79	0.064	14.3	11.5	9.8	59.20
0.9PdZn	44	4.74	0.073	14.9	14.4	9.3	64.32
1.0PdZn	38	5.20	0.089	15.2	12.2	9.4	75.10
1.1PdZn	37	3.79	0.054	14.4	13.2	10.1	51.20

N.B: S/A = Surface area, P.Width = Pore width, P. V = Pore volume

Table 2: XPS analysis data of freshly reduced catalysts

Catalysts	B.E. (eV) Pd (3d _{5/2})			Relative content of Pd Species (mol%)		
	Pd ⁰	Pd ²⁺ (PdO)	Pd ⁴⁺ (PdO ₂)	Pd ⁰	Pd ²⁺ (PdO)	Pd ⁴⁺ (PdO ₂)
0.7PdZn	335.4	336.3	337.8	83.	2.9	14.1
0.9PdZn	335.5	336.3	337.8	83.6	1.7	14.6
1.0PdZn	335.8	336.4	338.1	85.1	2.4	12.5
1.1PdZn	335.5	336.4	337.8	83.2	2.1	14.7

Table 3: Binding energies of deconvoluted Ce 3d spectra over the surface of catalysts.

Catalysts	Ce (3d _{5/2})					Ce (3d _{3/2})					
	v ⁰	v'	v	v'	v''	v'''	u ⁰	u	u'	u''	u'''
0.7PdZn	880.8	884.8	882.8	884.8	889.2	898.7	899.4	901.4	902.9	907.8	917.2
0.9PdZn	880.9	884.9	882.9	884.9	889.4	898.9	899.5	901.5	903.2	907.9	917.3
1.0PdZn	880.9	884.9	883.0	884.9	889.5	899.0	899.5	901.7	903.1	908.1	917.5
1.1PdZn	880.4	884.4	882.5	884.4	889.1	898.5	899.0	901.2	902.8	907.7	917.0

Table 4: Catalytic performance for CO₂ hydrogenation to methanol reaction.

Catalysts	CO ₂ Conversion (%)	CH ₃ OH Selectivity (%)	CO Selectivity (%)	STY (CH ₃ OH) (g/kg _{cat} /h)	Ref.
0.7PdZn	7.92	98.9	1.21	61.62	[This work]
0.9PdZn	10.79	96.4	3.60	82.50	[This work]
1.0PdZn	14.12	94.5	5.10	114.30	[This work]
1.1PdZn	9.77	93.6	6.41	72.08	[This work]
5Pd/ZnO/Al ₂ O ₃ ^a	7.8	50.1	49.9	-	[10]
5Pd/ZnO ^b	6.3	64.0	36.0	54.47	[15]
5PdZn/TiO ₂ ^c	10.1	40.0	59.0	45.50	[41]

Operating conditions (This work) T = 220°C, P = 20bar, H₂/CO₂ = 3:1, GHSV = 2400h⁻¹, CO₂ conversion, methanol selectivity and methanol STY are reported within ± 0.5, ± 0.3 and ± 0.2 standard deviations respectively for 1.0PdZn optimum catalyst). Reduction in H₂ (550°C, 1 hr), Catalyst loading = 0.5g, data collected after 3hrs.

[a] T = 220°C, P= 20bar, GHSV= 3600h⁻¹, [b] T = 250°C, P= 20bar, GHSV=3600h⁻¹, [c] T = 220°C, P= 20bar, GHSV= 3600h⁻¹.