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

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### **Graphical Abstract**



### Highlights

- 14% CO<sub>2</sub> conversion and 95% methanol selectivity were achieved over PdZn/CeO<sub>2</sub>
- 1.0PdZn/CeO<sub>2</sub> 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/CeO<sub>2</sub> catalysts prepared *via* sol-gel chelatization for the hydrogenation of CO<sub>2</sub> under mild reaction conditions. The formation of a PdZn alloy, which is the main active phase for this reaction, was maximized for the catalyst with a Pd to Zn ratio close to 1. For this catalyst, a maximum conversion of 14%, close to thermodynamic equilibrium, and high selectivity to methanol (95%) were achieved at 220 °C, 20 bar, 2400 h<sup>-1</sup> GHSV and H<sub>2</sub>:CO<sub>2</sub> 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 study confirmed the presence of Pd°, being maximum for the optimized catalyst composition. At lower temperature, i.e. 180 °C, 1.0PdZn catalyst showed 100% selectivity to methanol with 8% CO<sub>2</sub> conversion. RWGS reaction is responsible for the production of CO and its selectivity increases with temperature. *In situ* DRIFTS suggests that CO<sub>2</sub> is activated as adsorbed CO<sub>3</sub> species over CeO<sub>2</sub>. Surface micro-kinetics demonstrates that methanol can be formed either *via* formaldehyde or formic acid surface intermediates.

Keywords: PdZn alloy, CeO<sub>2</sub>, 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 CO<sub>2</sub> production [2]. In this spirit, Olah [3] proposed the "methanol economy", whereby atmospheric CO<sub>2</sub> (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/Al<sub>2</sub>O<sub>3</sub> catalyst at 250-300°C and 50-100bar [5, 6]. Unfortunately, the use of similar Cu-based catalyst for the hydrogenation of CO<sub>2</sub> requires excessive pressures to reach decent selectivity to methanol [7,8]. Meanwhile, it is crucial to note that, Cu supported on ZnO, ZrO<sub>2</sub>, and CeO<sub>2</sub> represents a promising alternative for the process. Metal-oxide centers formed by doping CeO<sub>x</sub> on metallic Cu(111) enhanced the chemical properties of CeO<sub>x</sub>/Cu(111) catalyst and consequently helped in improving the reaction pathway for methanol synthesis [9]. Also, the partial coverage of ZnO<sub>x</sub> on the surface of reduced Cu nanoparticles can form either Zn/Cu bimetallic alloy or ZnO-Cu interface, serving as the active sites for methanol synthesis reaction [10-12].

These challenges have opened research opportunities in the search for alternative catalysts for  $CO_2$  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 [13,14]. The formation of bimetallic alloys (PdZn, PdGa, PdZr) of Pd supported on ZnO, Ga<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> showed enhanced catalytic activity and selectivity to methanol compared to Pd/support alone [15-22]. Similarly, for methanol steam reforming (MSR), PdZn surface alloy and ZnPd intermetallic compounds (IMCs) are generally agreed upon to modify the adsorption properties of metallic Pd and enhance CO<sub>2</sub> selectivity and methanol conversion [23, 24, 25, 26]. Bahruji et al. studied the influence of PdZn particle size over CO<sub>2</sub> conversion and methanol selectivity [18, 27] and found that smaller particles, with a strong interaction with the support, resulting 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 [26]. Xu et al. [13] investigated different preparation methods of PdZn over Al<sub>2</sub>O<sub>3</sub> and reported that coprecipitation method is superior over deposition precipitation and impregnation methods in terms of methanol selectivity.

Supports like ZrO<sub>2</sub>, ZnO, SBA-15, MCM-48, Ga<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> have been tested as potential supports for Pd in CO<sub>2</sub> hydrogenation to methanol [13, 20, 28, 29, 30]. However, CeO<sub>2</sub> promotes CO<sub>2</sub> activation at the metal/support interface due to its ability to create surface and bulk oxygen vacancies [31]. Doping Ca on PdZn/CeO<sub>2</sub> catalysts improved surface basicity and subsequently assisted the reducibility of ceria by creating more oxygen vacant sites and enhanced catalytic activity [17]. Pd promotion in Cu/CeO<sub>2</sub> based catalysts improves the dispersion of Cu and overall catalytic activity [32, 33]. The high cost of Pd (\$40.58/gram) necessitates its optimized loading in catalysts.

Our group recently reported 5wt%Pd-5wt%Zn/CeO<sub>2</sub> (Pd:Zn molar ratio = 0.67) catalysts for CO<sub>2</sub> hydrogenation to methanol *via* sol-gel technique [17], where structural and textural properties of the catalyst can be controlled using this preparation method [34], showing enhanced activity and selectivity for this process. This research focuses on optimizing Pd:Zn molar ratio (0.7 to 1.1) over CeO<sub>2</sub> support prepared *via* citric acid (CA) chelatization method based on our previous finding, having the aim to improve the catalytic activity for methanol synthesis. The synthesized catalysts were characterized using BET, XRD, XPS, SEM/EDX, EELS-STEM, CO<sub>2</sub> TPD, H<sub>2</sub>-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<sub>2</sub> catalysts with varying Pd:Zn nominal molar ratio (0.7 to 1.1) were synthesized *via* sol-gel using CA as a chelating agent as reported in our previous report (CA:Metal molar ratio of 3:1) [17]. 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; Pd(NO<sub>3</sub>)<sub>2</sub>.xH<sub>2</sub>O to Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O salt to CA. Obtained Pd-Zn and Ce-CA solutions were mixed under stirring at 90°C.

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°C/min ramping rate) leaving behind the oxidic form of catalytic precursors.

#### 2.2. Characterization Methods

N<sub>2</sub>-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° = 0.05-0.3 and non-local density functional theory (NLDFT) equilibrium models of slit pore geometry. Pore volume was estimated from N<sub>2</sub> isotherms at a relative pressure of P/P° = 0.98 by utilizing the bulk liquid N<sub>2</sub> density.

Temperature programmed reduction (H<sub>2</sub>-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  $30^{\circ}$ C. TPR experiments were conducted from room temperature to  $800^{\circ}$ C under 20ml/min flow of 5%H<sub>2</sub>/N<sub>2</sub> mixture at a ramping rate of 10K/min, during which the H<sub>2</sub> consumption was recorded.

Temperature programmed desorption (CO<sub>2</sub>-TPD) analysis of all calcined samples was carried out using a micromeritics (AutoChem HP) chemisorption analyzer coupled with a mass spectrometer. Similar to TPR experiments, 0.1g of a sample was loaded into a u-type reactor. Prior to CO<sub>2</sub> adsorption, catalyst precursors were reduced at 550°C under H<sub>2</sub> 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% CO<sub>2</sub>/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  $0-110^{\circ}$  using an Equinox 1000 diffractometer (Co-k $\alpha$  radiation of 0.1709 nm wavelength).

X-ray photoelectron spectroscopy (XPS) was performed on a SPECS GmbH (Germany) with non-monochromatic Al-K $\alpha$  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<sup>-8</sup> mbar was reached. This is followed by transferring the sample into the analysis chamber under UHV pressure of 4.8 x 10<sup>-10</sup> 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 C-C bond was used as binding energy (B.E) reference for charge correction [35]. 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 800-4000cm<sup>-1</sup>. 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<sub>2</sub> 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<sub>2</sub>/H<sub>2</sub> mixture (or CO<sub>2</sub>) flow to determine the intermediate species formed at different reaction conditions (temperature and pressure). Spectra were obtained continuously by averaging 100 scans with 4cm<sup>-1</sup> 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 H<sub>2</sub> 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  $CO_2/H_2$  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 Qpacked column for TCD (H<sub>2</sub>, CO and CO<sub>2</sub> 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 CO<sub>2</sub> conversion were calculated using Eqs. (1-3).

CO<sub>2</sub> Conversion: 
$$X_{CO_2}(\%) = \frac{F_{CO_{2in}} - F_{CO_{2out}}}{F_{CO_{2in}}} * 100$$
 (1)

Methanol Selectivity:  $S_{MeOH}(\%) = \frac{F_{MeOH}}{F_{CO_{2_{in}}} - F_{CO_{2_{out}}}} * 100$  (2)

Methanol STY: 
$$STY_{MeOH} = \frac{Mass of MeOH (g)}{Catalyst weight (g) \times Hour}$$
 (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  $N_2$  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/P° is a characteristic which indicates the presence of mesopores smaller than 3.4 nm and bigger cavities in the catalyst structure [36, 37]. BET surface area of the reduced catalysts was determined in the range of 36-43 m<sup>2</sup>/g (Table 1). The pore volume of the fresh catalysts increased with increasing PdZn molar ratio from 0.05-0.09 cm<sup>3</sup>/g when PdZn ratio was increased from 0.7 to 1.0 and then observed a decrease in PV (0.05 cm<sup>3</sup>/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. CO<sub>2</sub>- TPD

TPD analysis of adsorbed CO<sub>2</sub> was conducted in He flow to understand the basicity of the *in situ* reduced catalysts (Fig. 2A). All the spectra exhibited low CO<sub>2</sub> desorption temperature with peaks in the range of 80-91°C, attributable to CO<sub>2</sub> physically adsorbed on the catalyst surface. Fan and Fujimoto [38] reported the possibility of CO<sub>2</sub> to decompose into CO over Pd/CeO<sub>2</sub> at low temperature. The amount of CO<sub>2</sub> desorbed from the catalyst surface for all samples ranged from 19.7-75  $\mu$ mol/g<sub>cat</sub> (Table 1). It appeared from the TPD profile of pure CeO<sub>2</sub> (19.68  $\mu$ mol/g<sub>cat</sub>) that the adsorption of CO<sub>2</sub> mainly happened on CeO<sub>2</sub>/Ce<sub>2</sub>O<sub>3</sub> interfacial site due to its high basicity and surface defects generated after reduction in H<sub>2</sub>. The presence of Zn in the vicinity of CeO<sub>2</sub> slightly increased CO<sub>2</sub>

adsorption on Zn/CeO<sub>2</sub> surface (21.56  $\mu$ mol/g<sub>cat</sub>). More so, in our previous report, the presence of PdZn alloy notably modified the basicity and oxygen vacancies of ceria leading to enhanced CO<sub>2</sub> adsorption capacity [17]. If we take the CO<sub>2</sub> desorbed amount as a measure of basicity, the catalyst 1.0PdZn showed the highest amount of basicity (75  $\mu$ mol/g<sub>cat</sub>) among the investigated catalysts and showed a superior catalytic performance (explained in the activity section 3.2.1). CO<sub>2</sub> peak around 90°C is attributed to the decomposition of b-HCO<sub>3</sub><sup>-</sup> while the shoulder peak around 210°C indicates b-CO<sub>3</sub><sup>2-</sup> and m-CO<sub>3</sub><sup>2-</sup> species [39], indicating that the surface oxygen vacancies of ceria can form carbonates species without any constraint. We have observed the CO<sub>3</sub><sup>2-</sup> formation in the DRIFT study (section 3.3) over CeO<sub>2</sub> support. As the catalysts were reduced *in situ* using hydrogen, H<sub>2</sub> is desorbed at 55-75 °C (*vide infra*) and is responsible for the formation of HCO<sub>3</sub><sup>-</sup>.

#### **3.1.3.** $H_2 - TPR$

The reducibility of the different catalysts was studied using H<sub>2</sub>-TPR (Fig.2B). A negative peak, which corresponds to the decomposition of palladium hydride (PdH<sub>x</sub>) was observed at the temperature range of 55-75°C over all the Pd-based catalysts [17, 27]. PdH<sub>x</sub> is unstable and usually decomposes during high temperature reduction, releasing hydrogen and subsequently producing a negative peak [40]. Alloying Pd with another metal can reduce the solubility of H<sub>2</sub> and consequently decrease the peak intensity of PdH<sub>x</sub> [41]. 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 CeO<sub>2</sub> support [42].

The broad peak centered at 370°C (Zn/CeO<sub>2</sub> sample) can be attributed to Zn-O-Ce surface interaction, in agreement with Venkataswamy et al. [43]. At such a temperature (370°C), the reduction of ZnO is impossible in the absence of Pd. However, it appears that the incorporation of Pd in Zn structure is responsible for the early partial reduction of Zn which otherwise is reported to start at 600°C [44]. In agreement with other authors, we observed the reduction of surface oxygen of ceria at about 400-530°C while bulk ceria reduction only occurs at about 800°C [17, 45]. Nevertheless, similar reduction peaks which are attributable to the partial reduction of surface CeO<sub>2</sub> are observed at 350-500°C for all the Pd:Zn samples and are in agreement with previous reports by Zhu et al. [46]. It can be deduced from the TPR spectra that the presence of Pd and Zn assist in decreasing the surface CeO<sub>2</sub> reduction temperature (also shown in Supplementary Figure SF 1). The influence of Pd in lowering the reduction of surface oxygen of ceria is well known [42, 46]. Pd has the ability to dissociate hydrogen at the surface and spillover H-adatoms unto CeO<sub>2</sub> surface, facilitating its reduction.

#### 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 Pd<sub>2</sub>Zn (110) was observed at 49° (specially for 1.1PdZn) [19]. Freshly reduced catalysts revealed two distinct diffraction

peaks at 48° (111) and 51.7° (200) respectively, corresponding to the formation of  $\beta$ -PdZn tetragonal crystal phase. These diffraction peaks appeared at about 42° and 44° respectively when Cu-k $\alpha$  radiation ( $\lambda = 0.0154$ nm) was used in previous reports [15, 18, 47].

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 CeO<sub>2</sub> (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  $\beta$ -PdZn phase is in the range of 11.5-15.2nm (Table 1). The calculated XRD peaks assignment for pure ceria and PdZn alloy are shown in the Supplementary Fig. (SF2).

#### 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 335.5-335.8. Deconvolution of these B.E. peaks shows that Pd is present as Pd<sup>0</sup>, Pd<sup>2+</sup> and Pd<sup>4+</sup> oxidation states (Table 2) in accordance with other reports [17, 35, 48]. The XPS analysis of Pd/CeO<sub>2</sub> (5wt% Pd) revealed the main peak of Pd  $(3d_{5/2})$  at a B.E. of 336.8eV, indicating the presence of PdO [49] (Supplementary Fig SF3). Deconvolution of this spectra revealed the presence of PdO [49] (Supplementary Fig SF3). Deconvolution of this spectra revealed the presence of Pd<sup>0</sup> at a B.E. of 335.2eV, which appears to be in the B.E. range for metallic Pd (335.0 - 335.2eV) [50, 51]. However, the PdZn/CeO<sub>2</sub> samples revealed a positive B.E. shift of 0.4-0.8eV for Pd<sup>o</sup> oxidation state (Table 2). The shift in Pd<sup>o</sup> oxidation state is due to the electron transfer from Pd(4d) to Zn(4d) and also hybridization of Pd(4d) and Pd(5s,5p) hence a decrease in electronic population in Pd and increasing the B.E. of Pd<sup>o</sup> [52] and also an indication of formation of PdZn alloy [53,54]. This finding is supported

by the identification of PdZn crystal phase over CeO<sub>2</sub> according to XRD analysis. The B.E. peak intensities of Pd<sup>o</sup> (in the form of PdZn alloy), shown in Table (2), increases with increasing Pd:Zn molar ratio (0.7 to 1.0PdZn samples), probably due to the of disruption of Pd and Zn interaction on exposure to air [53]. We estimated the relative amount of surface Pd<sup>o</sup> present on the catalysts to vary from 83- 85mol% with 1.0PdZn showing the highest concentration of Pd<sup>o</sup> species (Table 2). High concentration of surface Pd<sup>o</sup> 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 [55]. Meanwhile, core level Zn  $2p_{3/2}$  peak at 1022eV was identified (Supplementary Fig. SF4). 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. SF5). The presence of Zn Auger peak at 998eV revealed that most of the Zn present in the catalysts exist as  $Zn^{2+}$  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 [27, 56-58]. XPS spectra of O 1s for all catalysts revealed that main B.E. 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. SF6).

The main Ce  $(3d_{5/2})$  B.E. peak identified in the range of 882.6-883.3eV, corresponds to Ce<sup>4+</sup> (v doublet) and agrees with Matsumura et al. [35, 45]. 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 a shake-up and shake down characteristics in agreement with Bêche et al. [35, 59] and are shown in Fig. 5. Pairs of Ce<sup>3+</sup> doublets (v<sup>o</sup>, u<sup>o</sup>, u ' and v ') observed during XPS analysis confirms the occurrence of partial reduction of ceria (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. (SF7- SF10). 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 CeO<sub>2</sub>.

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. From the elemental maps for 0.7PdZn, 0.9 PdZn (in Supplementary Figure SF 11 & 12) and 1.0PdZn catalyst (Fig. 7), it is well evidenced that with the increase of Pd loading, the homogeneity of Pd and Zn distribution over CeO<sub>2</sub> was increased. From the Fig. 7 (1.0 PdZn), we can see the highest proximity of Pd and Zn among the analyzed samples, which may be caused by the Pd-Zn

alloy formation and showed superior activity compared to other catalysts. Also, high carbon contamination which is observed from microscopy data can be related to the remaining citric acid from the precursor solution.

Supplementary Fig. SF7- SF8 (d) display the mapping and phase diagram of other catalysts, confirming the non-uniform distribution of Pd and Zn species on the CeO<sub>2</sub> 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 [60]. 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<sup>-1</sup>) on the catalytic performance of the prepared catalysts for CO<sub>2</sub> hydrogenation to methanol was investigated and results are depicted in Fig. 8A. All the catalysts showed a rapid increase in CO<sub>2</sub> conversion until 250°C after that increase in conversion was slowed down, except for 1.0PdZn catalyst for which CO<sub>2</sub> conversion is higher compared to other samples, showing a linear increment of activity with temperature. The CO<sub>2</sub> conversion at 250°C and 270 °C, all the catalysts showed conversion values in between 77-88% of thermodynamic equilibrium value (Supplementary Table ST2 and Supplementary Figure SF13). The 1.0PdZn showed high activity (in all temperature range) compared to the other three catalysts having the closest value to the thermodynamic equilibrium conversion. The higher activity can be assigned to enhanced RWGS reaction

over this catalyst, showing high selectivity to CO compared to other catalysts (Fig 8B and Supplementary Figure SF13) specially at 250 °C and 270 °C. Methanol selectivity was observed to decrease with increasing reaction temperature due to the competing RWGS reaction (Fig. 8C). These observations are convened in a methanol selectivity – CO<sub>2</sub> conversion curve (Fig. 8D), which clearly shows that with the increase in reaction temperature, methanol selectivity decreases with increasing CO<sub>2</sub> conversion for all the tested catalysts. In summary, 220°C is the best temperature to operate and 1.0PdZn catalyst showed a CO<sub>2</sub> conversion of 14% and maximum methanol STY of 114g/kg<sub>cat</sub>/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% CO<sub>2</sub> conversion and 98% selectivity at 200°C and 8% CO<sub>2</sub> 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<sup>-1</sup> 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  $CO_2$  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<sub>cat</sub>/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 Pd<sup>o</sup> species, present as PdZn bimetallic alloy (XRD, XPS section) in the 1.0PdZn catalyst, which is the optimum Pd:Zn ratio over CeO<sub>2</sub> surface for this hydrogenation reaction for methanol synthesis.

The activity data can be well correlated to the surface basicity and relative content of Pd<sup>o</sup> (obtained from deconvoluted data of XPS) as presented in Fig. 10. The surface basicity is related to the CO<sub>2</sub> uptake amount ( $\mu$ mol/gm) from the CO<sub>2</sub> TPD study. Both the surface basicity and Pd<sup>o</sup> content went through a maximum for the 1.0PdZn catalyst which also showed the best activity of CO<sub>2</sub> conversion and high methanol STY.

#### 3.2.3. Stability of 1.0PdZn/CeO<sub>2</sub> 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<sup>-1</sup> GHSV) and shown in Fig. 11. Methanol selectivity reached steady state at approximately 3hrs and within the next 30hrs, some deactivation was observed (12.5% CO<sub>2</sub> conversion and 91.6g/kg<sub>cat</sub>/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 (Supplementary Fig. SF14) 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. It appears that PdZn/CeO<sub>2</sub> catalyst

is susceptible for water formation *via* RWGS and might significantly contribute to the deactivation through sintering. As the activity reached equilibrium after 30hrs (Fig. 11), the attained  $CO_2$  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  $CO_2$  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 (12,000 $h^{-1}$ ), the STY of methanol reached 304g/kg<sub>cat</sub>/h with CO<sub>2</sub> conversion and methanol selectivity of 7.4 and 100% respectively (Fig. 12A). In addition, at long residence time (lowest GHSV of 2400 $h^{-1}$ ), catalytic performance approaches thermodynamic limit revealing the highest CO<sub>2</sub> conversion of about 14.12% and lowest methanol STY of 114g/Kg<sub>cat</sub>/h. Although, for commercial operation, GHSV lower than 2,400 $h^{-1}$  may not be practically applicable from an economic standpoint since the methanol space time yield will be very low. Generally, as the GHSV increases, CO<sub>2</sub> conversion and CO selectivity decrease while methanol selectivity and STY increase. The decrease in CO<sub>2</sub> conversion can be attributed to a reduced amount of adsorbed CO<sub>2</sub> 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<sup>-1</sup> respectively (Fig. 12B). It showed that as pressure increases from 1-20bar, CO<sub>2</sub> 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 H<sub>2</sub> (with CO<sub>2</sub>:H<sub>2</sub>=1:3 feed) which may inhibit adsorption and reaction of CO<sub>2</sub> over the catalyst surface. At 1, 5, 10 and 15bar, we have a considerable amount of conversion with a very high selectivity to methanol. CO<sub>2</sub> conversion and methanol selectivity of 3% (±0.05) and 85% respectively with methanol STY (19.1g/kg<sub>cat</sub>/h) at atmospheric pressure is superior to Iwasa et al. [15] 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) CO<sub>2</sub> 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 CO<sub>2</sub> adsorption on 1.0PdZn catalyst

FTIR spectra of pure  $CO_2$  adsorbed over the 1.0PdZn catalyst in the temperature range of 50-250°C are displayed in Fig. 13. A high intensity band at 2361 cm<sup>-1</sup> was observed for the gas phase  $CO_2$ . Bands typical of symmetric and asymmetric bidentate surface carbonate (b- $CO_3^{2-}$ ) were observed at 1301-1310 and 1574 cm<sup>-1</sup> respectively, at low-temperature

range (50-100 °C) which apparently disappeared forming monodentate carbonate species  $(m-CO_3^{2-})$  at 1078cm<sup>-1</sup> at higher temperature [61]. IR bands of surface hydrogen carbonates  $(HCO_3^{-})$  were identified at 1030-1040 and 1397cm<sup>-1</sup>, probably due to the interaction of adsorbed CO<sub>2</sub> with surface Ce-OH species. It can be inferred that surface m-CO<sub>3</sub><sup>2-</sup> species are formed at high temperature via decomposition of  $HCO_3^{-}$  intermediates, as also observed in CO<sub>2</sub> TPD study.

#### 3.3.2. CO<sub>2</sub>/H<sub>2</sub> adsorption on pure ceria support

The adsorption of CO<sub>2</sub>/H<sub>2</sub> mixture over pure CeO<sub>2</sub> support was conducted at the optimal operating condition (220°C, 20bar) and results are depicted in two sections (Supplementary Fig. SF15). Bands attributable to linearly adsorbed CO (CO<sub>L</sub>) were identified at 2177 and 2053cm<sup>-1</sup>. Weak bands of formate species at 2848 and 2939cm<sup>-1</sup> were observed, which may arise due to the interaction of adsorbed CO and surface OH group, in agreement with Li et al. [62]. In addition, different vibrational modes of formate species were also identified at 1258 and 1357cm<sup>-1</sup>, while the bands around 1476cm<sup>-1</sup> are typical of carbonate species [63]. Band range of 1023-1062cm<sup>-1</sup> is attributed to *v*(CO) stretching of methoxy species on ceria surface containing different coordination geometry [61]. However, we observed no *v*(C-H) vibrational mode of methoxy species over the pure ceria support.

# **3.3.3.** CO<sub>2</sub>/H<sub>2</sub> adsorption over the 1.0PdZn catalyst with temperature and pressure variation

The effect of temperature on  $CO_2/H_2$  adsorption over the 1.0PdZn catalyst in the range of 100-220°C at 20 bar pressure was studied and the spectra are depicted in Fig. 14. At a low

temperature of 100°C, there was no evidence of molecular adsorption/formation of methanol. However, weak peaks of linearly adsorbed CO were observed (2076-2179cm<sup>-1</sup>), indicating that CO formation via dissociative adsorption of CO<sub>2</sub> is quite spontaneous over the 1.0PdZn catalyst. At higher temperatures ( $\geq$  150°C), bands typical of methoxy species (2867cm<sup>-1</sup>), and gaseous methanol (2948-3000cm<sup>-1</sup>) began to form showing increasing intensity with the increase of temperature, i.e. the IR peak intensities of methanol and methoxy species at optimal reaction condition (220°C, 20bar) varied more than five folds compared to the band intensities at 150°C.

The overlapping peaks in the band range of 2820-3000cm<sup>-1</sup> can be assigned to *v*(C-H) vibrational mode of methoxy species and methanol [61, 63], which were not observed over pure CeO<sub>2</sub> support. This indicates that the presence of Pd (its H-atom spillover ability) assisted the formation of intermediate methoxy species needed for methanol formation. Peaks concentrated in the band range of 1300-1640cm<sup>-1</sup> can be ascribed to different vibrational mode of surface mono and bidentate formate species[64-66]. Weak bands in the frequency region of 1684-1748cm<sup>-1</sup> are typical of molecularly adsorbed formic acid (HCOOH) and formaldehyde (HCHO) species, in agreement with Li et al. [61].

In the pressure variation experiment (1-20 bar, 220°C), we remarkably observed significant methanol formation rate at atmospheric pressure over the catalyst surface (Supplementary Fig. SF16). IR peak intensity of methanol was increased with increasing pressure up to 20 bar, in line with our experimental data. The peak intensity of methanol at 20bar varies more than three folds compared to 1bar. Also, the increasing peak intensities of linearly adsorbed CO is an indication that dissociative adsorption of  $CO_2$  is a direct function of pressure.

Conclusively, the formation of surface carbonate (CO<sub>3</sub><sup>-</sup>) species is the main step for activating CO<sub>2</sub> which occurs at the surface oxygen vacant sites of CeO<sub>2</sub>, i.e. the formation of Ce<sup>3+</sup> species during catalyst reduction at high temperature. Pd performs a dual role of activating and supplying hydrogen adspecies (H<sub>s</sub>) necessary for CO<sub>2</sub> hydrogenation and accelerating the kinetics of methanol formation. Observation of surface methoxy species, formaldehyde, and formic acid suggests two possible routes for methanol production, simultaneously happening over the surface (Fig. 15). 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 CeO<sub>2</sub> support for CO<sub>2</sub> hydrogenation to methanol has been studied. The catalyst with a 1:1 Pd:Zn molar ratio showed the optimum performance under reaction conditions at 220 °C, 20 bar and 2400 h<sup>-1</sup> GHSV, with the stoichiometric molar ratio 3:1 (H<sub>2</sub>:CO<sub>2</sub>), resulting in a methanol STY of 114g/kg<sub>cat</sub>/h. Interestingly, this catalyst is also active under atmospheric conditions with 3% CO<sub>2</sub> conversion, 85% methanol selectivity and 19.1g/kg<sub>cat</sub>/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-formic acid-methoxy species.

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**Fig. 1:** (A) BET isotherms and (B) pore size distribution curve calculated by NLDFT model for 0.7PdZn, 0.9PdZn, 1.0PdZn and 1.1PdZn catalysts reduced at 550°C for 1h **Fig. 2:** (A) (A) CO<sub>2</sub>-TPD spectra and (B) H<sub>2</sub>-TPR spectra of calcined catalysts (i) CeO<sub>2</sub> support (ii) ZnO/CeO<sub>2</sub> (iii) 0.7PdZn (iv) 0.9PdZn (v) 0.9PdZn (vi) 1.1PdZn

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Triangular phase diagram for the 1.0PdZn catalyst.

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Fig. 2: (A) CO<sub>2</sub>-TPD spectra and (B) H<sub>2</sub>-TPR spectra of calcined catalysts (i) CeO<sub>2</sub> support (ii) ZnO/CeO<sub>2</sub> (iii) 0.7PdZn (iv) 0.9PdZn (v) 0.9PdZn (vi) 1.1PdZn



Fig. 3: XRD patterns of (A) Calcined and (B) Freshly reduced catalysts for CeO<sub>2</sub> support, 0.7PdZn, 0.9PdZn, 1.0PdZn, and 1.1PdZn samples.



Fig. 4: XPS spectra of Pd (3d) for freshly reduced catalysts (A) 0.7PdZn (B) 0.9PdZn (C) 1.0PdZn (D) 1.1PdZn. (Doted lines represent the oxidation states of Pd species).



Fig. 5: XPS spectra of Ce (3d) for (A) 0.7PdZn, (B) 0.9PdZn, (C) 1.0PdZn, (D) 1.1PdZn (Red and black colors represent the B.E. peaks of  $Ce^{3+}$  and  $Ce^{4+}$  oxidation states respectively)



Fig 6: EDS elemental distribution mapping of (a) Pd (b) Zn (c) Pd-Zn and (d) Triangular phase diagram for 1.0PdZn catalyst.



Fig. 7: STEM image of 1.0PdZn catalyst.



Fig. 8: (A) CO<sub>2</sub> conversion, (B) CO selectivity, (C) Methanol selectivity as a function of reaction temperature, (D) Methanol selectivity versus CO<sub>2</sub> conversion over 0.7PdZn, 0.9PdZn, 1.0PdZn and 1.1PdZn catalysts (P = 20bar, GHSV = 2400h<sup>-1</sup>, H<sub>2</sub>/CO<sub>2</sub>=3, online data collection after 3hr.)



Fig. 9: (A) CO<sub>2</sub> conversion and methanol STY, (B) Product selectivity as a function of nominal Pd:Zn molar ratio (P = 20bar, T= 220°C, GHSV = 2400h<sup>-1</sup>, H<sub>2</sub>/CO<sub>2</sub>=3)



Fig. 10: Variation of (A) CO<sub>2</sub> conversion with surface relative content of Pd<sup>o</sup> (XPS), (B) CO<sub>2</sub> conversion with CO<sub>2</sub> uptake (TPD), (C) Methanol STY with surface relative content of Pd<sup>o</sup> (XPS), and (D) Methanol STY with CO<sub>2</sub> uptake (TPD) for all catalysts (T = 220°C, P=20 bar, GHSV=2400h<sup>-1</sup>).



Fig. 11: Activity performance of 1.0PdZn during time on stream (TOS) experiment.



Fig. 12: Catalytic performance of 1.0PdZn catalyst at varying (A) GHSV, (B) Reaction pressure (T =  $220^{\circ}$ C and H<sub>2</sub>/CO<sub>2</sub> = 3:1).



Fig. 13: Infrared spectra of  $CO_2$  adsorption over 1.0PdZn catalyst at 1 bar with increasing temperature: (a) 50°C (b) 100°C (c) 150°C (d) 200°C (e) 250°C



Fig. 14: Infrared spectra of  $CO_2/H_2$  adsorption over 1.0PdZn catalyst at 20bar and increasing temperature: (a) 100°C (b) 150°C (c) 180°C (d) 220°C (After 1hr of operation at each temperature).



Fig. 15: Reaction mechanism of methanol formation from CO<sub>2</sub> hydrogenation over 1.0PdZn catalyst.

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	N	l2 physisorpt	ion	XR	CO <sub>2</sub> TPD		
Catalysts	BET S/A	P. Width	P. V	PdZn(111)	PdZn(200)	CeO <sub>2</sub> (111)	CO <sub>2</sub> Desorbed
	$(m^{2}/g)$	(nm)	$(\text{cm}^{3}/\text{g})$	(nm)	(nm)	(nm)	$(\mu mol/g_{cat})$
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

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

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

Table 2: XPS analysis data of freshly reduced catalysts

		B.E. (eV) Po	Relative content of Pd Species (mol%)				
	]	Pd <sup>o</sup>					
Catalysts	Pd <sup>o</sup> (Pd in PdZn alloy)	Shift from Metallic Pd <sup>o</sup> (335.0 eV)	Pd <sup>2+</sup> (PdO)	Pd <sup>4+</sup> (PdO <sub>2</sub> )	Pd°	Pd <sup>2+</sup> (PdO)	Pd <sup>4+</sup> (PdO <sub>2</sub> )
0.7PdZn	335.4	+0.40	336.3	337.8	83.0	2.9	14.1
0.9PdZn	335.5	+0.50	336.3	337.8	83.6	1.7	14.6
1.0PdZn	335.8	+0.80	336.4	338.1	85.1	2.4	12.5
1.1PdZn	335.5	+0.5	336.4	337.8	83.2	2.1	14.7

NB: The metallic Pd<sup>o</sup> B.E. is taken as 335.0 eV[50].

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

Catalysts	Ce (3d <sub>5/2</sub> )					Ce (3d <sub>3/2</sub> )						
	vo	v'	v	v'	<b>v</b> "	v'''	u <sup>o</sup>	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	

Catalysts	CO <sub>2</sub>	CH <sub>3</sub> OH	СО	STY	Ref.
	Conversion	Selectivity	Selectivity	(CH <sub>3</sub> OH)	
	(%)	(%)	(%)	(g/kg <sub>cat</sub> /h)	
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]
1.0PdZn <sup>*</sup>	14.07	97.2	2.81	165.85	[This work]
5Pd/ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	7.80	50.1	49.9	-	[13]
5Pd/ZnO <sup>b</sup>	6.30	64.0	36.0	54.47	[18]
5PdZn/TiO <sub>2</sub> <sup>c</sup>	10.10	40.0	59.0	45.50	[57]
0.25Pd-Cu/SiO <sub>2</sub> <sup>d</sup>	6.70	30.0	70.0	32.30	[67]

Table 4:	Catalytic	performance	for	$CO_2$	hydrog	genation	to	methanol	reaction.
	2	1				0			

Operating conditions (This work)  $T = 220^{\circ}C$ , P = 20bar,  $H_2/CO_2 = 3:1$ ,  $GHSV = 2400h^{-1}$ , Reduction in  $H_2$  (550°C, 1 hr), Catalyst loading = 0.5g, data collected after 3hrs, 1.0PdZn\* = Catalyst testing at 3600h<sup>-1</sup>, Equilibrium methanol yield = 11%, and equilibrium conversion = 18.3%. CO<sub>2</sub> conversion, methanol selectivity and methanol STY are reported within  $\pm$  0.5,  $\pm$  0.3 and  $\pm$  0.2 standard deviations respectively for 1.0PdZn optimum catalyst). [*a*] T = 220°C, P= 20bar, GHSV= 3600h<sup>-1</sup>, [*b*] T = 250°C, P= 20bar, GHSV=3600h<sup>-1</sup>, [*c*] T = 220°C, P= 20bar, GHSV= 3600h<sup>-1</sup>, [*d*] T = 250°C, P= 41bar, GHSV=3600h<sup>-1</sup>