**Mesoporous NanocrystallineTiO₂ Supported Metal (Cu, Co, Ni, Pd, Zn, and Sn) Catalysts:
Effect of Metal-Support Interactions on Steam Reforming of Methanol**

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Abstract

Mesoporous TiO₂supported Cu, Co, Ni, Pd, Sn and Zn catalysts (M-TiO₂) were synthesized using facile one-step synthesis method and were characterized using BET, XRD, TGA-DSC, TEM, SEM-EDX, ICP-OES, and H₂-TPR studies. The catalysts were further tested for steam reforming of methanol (SRM) to investigate their comparative catalytic performance. Depending on the nature of the metal component, the catalysts exhibited surface area, pore sizes, and TiO₂ crystallite sizes in the range of 99-309 m²/g, 2.63-4.69 nm and 6.8-17.2 nm, respectively. N₂-physorption, TGA-DSC and XRD analysis demonstrated that the presence of metal in the TiO₂ matrix stabilized the mesoporous structure by hindering the crystal growth during heat treatment and thereby preventing the collapse of porous structure. Furthermore, the characterization of 5-20% Zn-TiO₂ catalysts indicated that there exist an optimum Zn loading to obtain highest surface area which was found to be 15% in the present study giving a high surface area of ~258 m²/g. This was consistent with the SRM studies where the activity increased up to 15% and then decreased significantly with further increase in Zn loading to 20%. The results of the SRM studies coupled with extensive TPR analysis of different M-TiO₂ catalysts suggest that the specific metal-support interactions play a crucial role in controlling its performance on H₂ production. The SRM activity order for different metals incorporated in mesoporous TiO₂ was observed to be: Pd > Ni > Zn > Co >> Cu >> Sn. The Zn-TiO₂ catalyst showed the lowest CO selectivity among the different catalysts studied.

Keywords: Mesoporous TiO₂; Porous Structure Stabilization; Metal-support Interactions; Cu, Co, Ni, Pd, Sn, Zn-TiO₂; TPR; Hydrogen Production; Steam Reforming.

1. Introduction

The increasing global energy demand and environmental crisis due to incessant use of fossil fuels has stimulated research for a clean and efficient source of energy for both mobile and stationary applications in the form of fuel cells[1, 2]. Proton exchange (also called polymer electrolyte) membrane fuel cells (PEMFC) which mainly use hydrogen (H_2) as fuel are considered to be the most promising among different types of fuel cells[3-5]. Therefore, H_2 is likely to play a crucial role in the energy portfolio of future in the form of H_2 economy. Although hydrogen is potentially an ideal energy carrier, it is extremely difficult to store and transport. The effective exploitation of H_2 as an energy carrier will need a massive development in storage, transportation and distribution infrastructure. Thus, the production of hydrogen *insitu* using an on-board steam reformer for fuel cells in various transportation applications is a subject of great interest in the scientific community[6]. Not only it can eliminate the hydrogen storage and transportation safety concerns but allow the use of present gasoline distribution infrastructure for supply of reforming feed-stocks such as methanol and ethanol. However, in order for on-board H_2 production to be a reality, development of economical, effective and efficient steam reforming catalysts is one of the important challenges that still need to be addressed.

The nature of support material and its physical state strongly influence the activity and selectivity of steam reforming reactions. A wide range of support materials have been investigated for steam reforming reactions including Al_2O_3 , ZrO_2 , CeO_2 , Y_2O_3 , La_2O_3 , ZnO , TiO_2 and MgO [7-9]. A careful review of the literature shows that, although TiO_2 has been used extensively in photo-catalysis for photo-degradation of various pollutants and is well known for its unique metal-support interactions showing excellent catalytic properties [10-12], limited comprehensive studies have been reported for TiO_2 supported metal catalysts in hydrogen

production via steam reforming reactions [13-17]. More specifically, the influence of metal-support interactions on steam reforming activity and selectivity has not been studied in detail. Pinzari et al. [13] synthesized Zn/TiO₂ catalysts using impregnation method that yielded surface area in the range of ~15-80 m²/g depending on Zn loading. The highest activity was obtained with 5% Zn at 400 °C. Nichele et al. [14] investigated the Ni/TiO₂ catalysts prepared by two routes involving impregnation of Ti(OH)₄ and TiO₂. Both, the preparation method and calcination temperature strongly influenced the catalyst properties (surface area 2-82 m²/g) and subsequent ethanol steam reforming activity due to their pivotal role in establishing the strong-metal-support-interactions (SMSI). In their most recent studies [15], they compared the performance of Ni, Co and Cu metals supported on TiO₂ for ethanol steam reforming. Ni/TiO₂ showed significantly higher activity compared to Co/TiO₂ and Cu/TiO₂. The highest activity of Ni was attributed to its ability of C-C bond cleavage. The tendency of Ni deactivation due to coke formation was shown to be significantly controlled by tuning the interactions between Ni and TiO₂ via catalyst preparation. Thus, in addition to the nature of support material, the catalyst preparation method [18, 19] and type of the active metal component [20-22] can have profound influence on steam reforming performance of catalysts.

In order to have a better understanding of the metal-support interactions, we have synthesized metal nanoparticles supported on high surface area mesoporous TiO₂ catalysts using facile one-step procedure developed in our laboratory. Six metal components - Cu, Co, Ni, Pd, Sn and Zn, reported to be active for steam reforming reactions, were incorporated in mesoporous TiO₂ to obtain different M-TiO₂ catalysts. These catalysts were extensively characterized by different techniques including temperature programmed reduction (TPR) studies and tested for steam reforming of methanol (SRM) to understand the comparative role of different metals and

their interactions with TiO₂ on reaction activity and selectivity. To the best of our knowledge, no such systematic studies have been reported using one-step synthesis of high surface area mesoporous TiO₂supported Cu, Co, Ni, Pd, Sn and Zn catalysts.

2. Experimental

2.1. Materials and Methods

Titanium (IV) isopropoxide, 98+% (TIPR) and ammonium hydroxide, reagent ACS were obtained from Acros Organics, New Jersey, USA. Hexadecyltrimethylammonium bromide minimum, 99% (CTAB), Cu (II) nitrate hydrate, 98% ACS reagent, cobalt (II) chloride hexahydrate, zinc nitrate hexahydrate 98%, tin chloride dehydrate 98%, and palladium nitrate hydrate were procured from Sigma-Aldrich, Missouri, USA. Nickel nitrate, hydrofluoric acid, ethanol anhydrous and acetone, ACS reagent were purchased from Fischer Scientific, New Jersey, USA. All materials used were analytical grade and used without further purification. The water used at all stages of the experiments was purified using a Mill-Q Advantage A10 with Elix 5 system obtained from Millipore Corporation (Bedford, MA, USA).

2.2. Experimental Procedure

Mesoporous TiO₂ containing metal particles, M-TiO₂ (M: Cu, Co, Ni, Pd, Sn, and Zn) were synthesized using the reactants molar ratio of 1 TIPR: 0.52 CTAB: 282 H₂O: 26.21 ethanol. Several preliminary experiments were carried out to finalize most favorable synthesis parameters and procedure reported in this study. The quantities of the metal precursors used were determined to obtain 10wt% loading for different M-TiO₂ catalysts and 5-20wt% loading for Zn-TiO₂. While the % metal loading refers to the wt% loading, TiO₂ denotes the mesoporous TiO₂ in rest of this article. In a typical synthesis, a measured quantity of CTAB was added to a water-ethanol solution with 4/1 (water/ethanol) volumetric ratios and stirred for 30 min to get a clear

solution. In another beaker, a solution of metal salt in ethanol was prepared. After stirring for 30 min, this solution was mixed with CTAB solution and stirred again. To the resulting solution, a measured quantity of TIPR was added slowly and drop-wise with continuous vigorous stirring. The stirring was continued for another 30 min after TIPR addition. Then NH_4OH was added drop-wise to adjust the pH of solution to ~ 10 . The resulting mixture was stirred for 24 h at room temperature. The precipitate was washed with water until the pH of filtrate reached close to 7. The precipitate was then washed with ethanol and filtered. The filtered material was air dried for 24 h followed by oven drying at 110°C for 24 h. Finally, the dried material was calcined at 350°C for 5 h with a heating and cooling rate of $2^\circ\text{C}/\text{min}$ to remove the traces of templating material and to obtain crystalline TiO_2 .

2.3. Catalyst Characterization

The catalysts were extensively characterized to study their physical and chemical properties using different techniques including N_2 physisorption, small and wide angle X-ray diffraction (XRD), thermo-gravimetric and differential scanning calorimetric analysis (TGA-DSC), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), inductively coupled plasma optical emission spectroscopy (ICP-OES), and temperature programmed reduction (TPR).

TGA–DSC of the different catalyst samples under air flow (100 ml/min) was carried out using SDT Q600 V20.4 Build14 system (TA instruments, New Castle, DE, USA). The as-prepared catalyst sample was placed in an alumina crucible and heated under air at $10^\circ\text{C}/\text{min}$ from ambient to desired temperature. N_2 adsorption-desorption technique was used to determine Brunauer-Emmett-Teller (BET) surface area, pore size and pore volume of the catalysts samples. The N_2 adsorption/desorption isotherms were measured at liquid nitrogen temperature of -196.14

°C using Quantachrome NOVA 2200e instrument (Quantachrome Instruments, Boynton Beach, FL, USA). Samples were thoroughly degassed at 150 °C for several hours before the adsorption measurements. The total pore volume was derived based on the amount of N₂ adsorbed at a relative pressure close to one. Barrett-Joyner-Halenda (BJH) method was applied to the desorption branch of N₂ isotherms to determine the pore size distribution (PSD) and average pore diameters [23].

Powder XRD patterns of the catalyst samples were obtained using D8 DISCOVER X-ray diffractometer from Bruker (Bruker Optics, Inc., Billerica, MA) equipped with a PSD detector using Cu K α radiations generated at 40 mA and 40 kV at 0.014°/s scan speed. Scherrer's formula (Eq.(1)) was used to determine the sizes of TiO₂ and metal crystallites from full-width-half-maximum of respective XRD peaks.

$$\tau = \frac{0.9\lambda}{\beta \cdot \cos \theta} \quad (1)$$

The actual elemental composition of the calcined catalysts was determined by an ICP-OES (Agilent 710-ES) technique. A mixture of 2 ml hydrofluoric acid (51%) and 3 ml nitric acid (68%) was used to dissolve the 75 mg catalyst sample at 80 °C. Fourier transform infrared (FTIR) measurements were recorded on KBr pellets with Shimadzu IR Prestige-21 Fourier transform infrared (FTIR) 8300 spectrometer equipped with mercury-cadmium-telluride (MCT) detector. Zeiss Libra 120 (©Carl Zeiss NTS GmbH, Oberkochen, Germany) instrument operating at 120 kV was used to obtain the high resolution transmission electron microscopy (HRTEM) images of the catalyst samples. For the analysis, the catalyst sample particles were dispersed in ethanol with the help of ultrasonication and then dropped onto a holey-carbon-coated copper microgrid. Elemental mapping showing the dispersion of different metals in the M-TiO₂ catalysts was carried out on Zeiss EVO LS10 SEM equipped with OXFORD INCA X-act detector. For

the analysis, powdered samples were mounted on aluminum stubs with the help of two sided carbon tape. H₂-TPR experiments were performed on AutoChem II 2920 Chemical Analyzer equipped with thermal conductivity detector (TCD) from Micromeritics Instrument Corp. (Norcross, GA, USA). Prior to TPR analysis, the catalyst were degassed at 200 °C for 30 min in Argon (Ar) stream. The TPR profiles were recorded in the flow of 10% H₂/Ar gas mixture at 50 ml/min, and the temperature was raised up to 900 °C with a heating rate of 10 °C/min.

2.4. Catalysts Testing

Methanol steam reforming experiments to examine the performance of different TiO₂ supported catalysts were carried out in a tubular stainless steel packed bed reactor (6.22 mm internal diameter) in the range of 150–350 °C. A catalyst and sand (white quartz, 50–70 mesh) mixture (2:1 volume ratio) was packed into the reactor with quartz wool placed at both ends. The calcined catalyst was first reduced *ex-situ* in a tubular furnace for 2 h and then *in-situ* in the reactor for 1 h using 4% H₂/Ar at 350 °C. A methanol/water mixture was fed to the reactor using a HPLC pump via a vaporizer set at 350 °C. The reactor outlet stream was passed through a condenser to separate unreacted reactants from the non-condensable product gases. While the reaction temperature was varied in the range of 150–350 °C, gas hourly space velocity (GHSV) and methanol to water mole ratio were kept constant at 2838 h⁻¹ and 3:1, respectively, for all the experiments. The reaction products and collected condensate were analyzed by Agilent 7890B gas chromatography system. The gaseous products were separated using Restek ShinCarbon (2 m x 2 mm x 1/8”) packed column and analyzed on thermal conductivity detector (TCD) using Argon as a carrier gas. Condensate mixture carried using He gas was separated on Agilent DB-1 (60 m x 250 µm x 1 µm) capillary column and analyzed on flame ionization detector (FID). While the conversion of methanol is obtained using methanol material balance based on feed and

condensate (**Eq.(2)**), the productselectivitiesare determined by hydrogen (**Eq.(3)**) and carbon (**Eq.(4)**) balance among the different non-condensable products.

$$X_{Methanol} = \frac{CH_3OH \text{ moles converted}}{CH_3OH \text{ moles fed}} \times 100\% \quad (2)$$

$$S_{H_2} = \frac{H_2 \text{ moles in product}}{H_2 \text{ moles in product} + 2 \times CH_4 \text{ moles in product}} \times 100\% \quad (3)$$

$$S_{CO/CO_2/CH_4} = \frac{CO/CO_2/CH_4 \text{ moles in product}}{(CO_2 + CO + CH_4) \text{ moles in product}} \times 100\% \quad (4)$$

3. Results and Discussion

3.1. Thermal and Calorimetric Analysis of M-TiO₂Samples

Fig. 1a shows the representative TGA-DSC profiles of TiO₂ and 10%Co-TiO₂ recorded in air. TGA profiles for both the samples showed two weight loss stages. The first one is located below 200 °C and is associated with an endothermic peak centered at ~85 °C. This weight loss is attributed to the removal of adsorbed water on the surface of TiO₂. The second weight loss observed in the range of 200 to 400 °C coincided with an exothermic peak between 220-300 °C in the DSC profile and is due to the exothermic decomposition of CTAB which was used as the templating agent. In addition, 10%Co-TiO₂ sample showed a second small exothermic peak at about 300 °C that is ascribed to the decomposition of metal precursor (in this case, CoCl₂) [24]. The exothermic peaks of the DSC profiles centered at ~450 °C and ~510 °C, both associated with insignificant weight loss, observed for TiO₂ and 10%Co-TiO₂, respectively, are attributed to the phase change of TiO₂ from amorphous to crystalline state [25]. It can be further noticed that the crystallization temperature of TiO₂ increased from ~450 to ~500 °C upon addition of cobalt.

Fig. 1. TGA-DSC profiles of (a) TiO₂ and 10%Co-TiO₂ and (b) 5-20%Zn-TiO₂ catalyst samples

The TGA-DSC profiles of different Zn-TiO₂ catalysts with 5-20% Zn loading are shown

Fig. 1b. The general behavior of the profiles is similar to that described in **Fig. 1a**. However, two conspicuous features were observed in **Fig. 1b**; first, a consistent decrease in the intensity of

exothermic peak in the range of 240-340 °C and second, a shift in the crystallization temperature to higher values with increase in the Zn loading. The Zn-TiO₂ sample with 5% loading has a crystallization temperature of ~500 °C, which increased to ~560 °C with 20% loading. The decreased peak intensity at higher Zn loading indicates the presence of lower CTAB in the as-prepared samples due to its replacement by Zn. The consistent delay in the crystallization temperature of TiO₂ with increase in Zn loading will be discussed in more detail in the subsequent sections (3.2 and 3.3).

3.2. X-ray Diffraction Analyses of Different M-TiO₂ Catalysts

Fig.2 presents the XRD patterns of different calcined M-TiO₂ samples. TiO₂ exists in three different crystalline phases: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic).

Fig. 2. X-ray diffraction patterns for different M-TiO₂ catalyst samples.

The XRD pattern of TiO₂ clearly shows well-resolved, sharp peaks at 25°, 38°, 48°, 55°, 63° corresponding to the (101), (004), (200), (105), and (211) diffraction planes, respectively, of

anatase structural phase (JCPDS# 21-1272). However, addition of a metal led to a decrease in intensity of these peaks, indicating a lower degree of crystallinity. This decrease in crystallinity appeared to strongly depend on the type of metal incorporated in TiO_2 . For example, while the addition of Cu showed no significant change in intensities, the presence of Ni yielded very low intensity broad peaks corresponding to the anatase phase. The XRD spectrum of 10% Cu- TiO_2 exhibits two peaks at 2-theta 35.5° and 38.7° , ascribed to the CuO crystal phase, assigned to (002) and (111) planes (JCPDS# 80-1917), respectively. The XRD spectrum of 10% Pd- TiO_2 showed peaks at 2-theta values of 33.6° and 42° assigned to (002) and (110) crystalline planes, respectively, of tetragonal PdO (JCPDS# 75-584).

Fig. 3. X-ray diffraction patterns for Zn- TiO_2 catalysts with 5-20% Zn loading.

The XRD patterns of 10% Co- TiO_2 , 10% Zn- TiO_2 , 10% Ni- TiO_2 , and 10% Sn- TiO_2 samples showed no peaks that can be attributed to the metal or metal oxides. This could be due to one or more reasons which include the non-crystalline nature of particles, highly uniform

dispersion, preferential orientation of particles and very small sizes making them X-ray-amorphous. **Fig.3** shows the XRD spectra of Zn-TiO₂ catalyst samples illustrating the crystallization behavior of TiO₂ with Zn loading varying from 5-20%. As observed with other metals, the addition of Zn to TiO₂ matrix resulted in decreased peak intensities, owing to the lower crystallinity of TiO₂. It clearly indicates that the presence of metal atoms hinder or delays the TiO₂ crystallization process, which was corroborated by the TGA-DSC studies.

The rate of crystallization during heat treatment depends on the rate of atomic diffusivity of titanium ions. However, the presence of metal atoms could be acting as an impurity or adatoms decreasing the mobility of Ti ions resulting in decreased diffusivity and subsequent decreased crystallization [26, 27]. The sizes of TiO₂, CuO and PdO crystallites determined using Scherrer equation are shown in **Table 1**. The decreased sizes of TiO₂ crystals upon metal loading further confirmed the lower crystallinity. For instance, the average TiO₂ crystallites size of ~17.2 nm decreased by more than 50% to ~4-9.8 nm upon metal addition. The extent of decreased crystallinity was also observed to be dependent on the metal type and loading.

3.3. N₂-Physisorption Analysis to Study Textural Properties of M-TiO₂

The N₂ adsorption-desorption isotherms for TiO₂ and different M-TiO₂ samples with 10% metal loading are depicted in **Fig.4(A)**. All isotherms resembled the Type IV isotherm, a typical characteristic for mesoporous materials, based on IUPAC classification [28].

Fig. 4. (A) N₂ adsorption-desorption isotherms, and (B) BJH pore size distribution for different M-TiO₂ catalyst samples.

The hysteresis loop associated with isotherms is attributed to the capillary condensation which also confirms the presence of mesoporous structure. While TiO₂ isotherm showed a H2 type hysteresis loop corresponding to the ink bottle shaped pores, the shape of the hysteresis loop changed from H2 to H4 upon incorporation of metal particles, indicating a significant change in the textural properties. The H4 type hysteresis loops generally correspond to the slit-like pores. A sharp rise in N₂ uptake at relative pressure above 0.95 is due to the N₂ condensation in inter-particle pores. **Figure 4(b)** depicts the BJH pore size distribution of different M-TiO₂ catalysts indicating reasonably narrow distribution in the range of 3 to 4 nm. **Table 1** summarizes the BET surface areas, pore sizes, and pore volumes of the different M-TiO₂ catalyst samples investigated in this study. TiO₂ showed a high surface area of 146.6 m²/g, pore size of 4.7 nm and pore volume of 0.17 cm³/g. However, depending on the type of metal incorporated in TiO₂, the surface area, pore diameter, and pore volume varied significantly in the range of 99.7-309.8 m²/g, 2.53-4.93 nm, and 0.08-2.03 cm³/g, respectively, indicating a strong influence of the metal ions on TiO₂ textural properties. For instance, while the incorporation of Pd in TiO₂ significantly decreased the surface area by about 32%, the addition of Co remarkably increased it by about 111% to 309.8 m²/g.

The increase in surface area of M-TiO₂ samples with the addition of metals is similar to that reported by Youn et al.[29] who observed that the addition of small quantity of metal ions promoted the textural stability of mesoporous ZrO₂ resulting in an increased surface area. However, the underlying reasons were not discussed in detail. We believe that the effect of metal incorporation on the textural properties of mesoporous TiO₂ is linked to the influence of metal ions on the crystallization behavior of TiO₂ that was also observed in the TGA-DSC and XRD studies described in previous sections. Crystallization of mesoporous TiO₂ upon calcination leads to the loss of the mesoporous structure due to the increased crystallite sizes, thus decreasing the surface area [27]. The degree of decreased surface area depends upon the degree of crystallization. Thus, the higher surface area of M-TiO₂ compared to TiO₂ can be attributed to relatively lower extent of crystallization upon metal addition. However, this effect was not observed in 10%Pd-TiO₂ sample, where the specific surface area decreased upon addition of Pd compared to TiO₂ itself. The observed contradictory influence of Pd compared to other metals on M-TiO₂ surface area can be explained on the basis of its crystal sizes. The significantly larger Pd crystal sizes of about 49.4 nm (**Table 1**) could be responsible for the collapse of TiO₂ mesoporous structure leading to a reduction in surface area.

The textural properties of Zn-TiO₂ catalyst samples with different metal loadings of 5-20% are also presented in **Table 1**. An interesting behavior was observed in surface area variation when the Zn loading was increased from 0 to 20%. The surface area increased from ~146 to ~257.5 m²/g with the increase in Zn loading from 0 to 15%. However, further increase in Zn loading to 20% resulted in a drastic reduction in surface area to 140.1 m²/g. The first trend in surface area variation can be explained on the basis of delay in crystallization of TiO₂ due to the presence of Zn atoms, as discussed above and evident in TGA-DSC results (**Fig. 1b**). The Zn

atoms hinder the crystallization of TiO_2 avoiding the collapse of mesoporous structure up to 15% loading. However, when the Zn loading is increased to 20%, Zn atoms could be interfering with the formation of mesoporous structure itself. Thus, the observed lower surface area for 20% Zn- TiO_2 compared to TiO_2 can be attributed to the lack of mesoporous structure.

3.4. Chemical Composition Analysis using ICP-OES

The metal loadings in M- TiO_2 samples, determined using ICP-OES analysis, are shown in **Table 1**. The metal loadings varied in the range of 10.6 to 13.9% except for samples of 10% Sn- TiO_2 and 10% Pd- TiO_2 . For Sn and Pd catalysts, the loading was found to be considerably lower (5.26 and 5.32%) than the intended loading of 10%. While, the higher loading of metal can be attributed to the more loss of titania particles or precursor, the lower metal loading in some cases could be due to the loss of metal particles or precursors during the catalysts preparation.

3.5. FTIR Analysis

Fig. 5a and b show the FTIR spectra of typical as-prepared and calcined samples of TiO_2 and 10% Zn- TiO_2 , respectively.

Fig 5. FTIR spectra of as-prepared and calcined samples of: (a) TiO₂ and (b) 10%Zn-TiO₂.

A doublet band centered at $\sim 2920\text{ cm}^{-1}$ and $\sim 2854\text{ cm}^{-1}$ observed in both as-prepared samples and a broad high intensity band at about 1470 cm^{-1} in 10%Zn-TiO₂ sample (this band seems to be overlapped in wide band between $1520\text{--}1720\text{ cm}^{-1}$ for TiO₂ sample) corresponds to the symmetric -CH and asymmetric -CH₂ vibrations of the organic template, CTAB, that disappeared upon calcination confirming its complete removal by combustion[30]. The strong band in the range of $900\text{--}400\text{ cm}^{-1}$ is associated with vibration modes of Ti-O in TiO₂[31]. While, the broad adsorption bands in the range of $3800 - 3000\text{ cm}^{-1}$ are assigned to the stretching vibrations of -OH from physisorbed water molecules, the adsorption band around $\sim 1630\text{ cm}^{-1}$ is ascribed to the -OH bending vibrations arising from coordinated water on support surface [32]. The adsorption bands $\sim 2350\text{ cm}^{-1}$ correspond to atmospheric CO₂.

3.6. Microscopic Analysis of M-TiO₂ catalysts

Fig. 6 shows the representative TEM images of the calcined TiO_2 and M-TiO_2 samples. **Fig.6(a-c)** clearly show that both TiO_2 and M-TiO_2 have disordered but highly mesoporous structure indicating that the porous structure is intact after incorporation of 10% metal in one-step synthesis procedure. The sizes of the pores ranged between 2.5 nm to 5 nm confirming the results of N_2 -physisorption studies. The dark spots in the high contrast TEM image shown in **Fig.6d** indicate the uniform distribution of the cobalt particles in TiO_2 matrix. The SEM images of different calcined M-TiO_2 catalysts with metal mapping acquired using EDX analysis are shown in **Fig.7**. The sizes of the bulk catalyst particles varied in the range of 2-40 μm . The significant differences in the dispersion of different metals in TiO_2 support are clearly evident from visual inspections. The highest dispersion was observed for 10%Co- TiO_2 which was followed by 10%Pd- TiO_2 . While Ni- TiO_2 and Sn- TiO_2 showed similar but relatively moderate dispersion, the least dispersion was noticed in Zn- TiO_2 and Cu- TiO_2 samples. The clarification of these observations is further bolstered by TPR results discussed in the following section.

Fig. 6: TEM images of (a) TiO₂ (b) 10%Sn-TiO₂ (c) 10%Zn-TiO₂ and (d) 10%Co-TiO₂.

Fig. 7. SEM images with EDX elemental mapping for (a) 10%Cu-TiO₂ (b) 10%Co-TiO₂ (c) 10%Ni-TiO₂ (d) 10%Pd-TiO₂ (e) 10%Sn-TiO₂ and (f) 10%Zn-TiO₂

3.7. Effect of Metal-Support Interaction on Reduction Behavior of M-TiO₂ Catalysts

TiO₂ is known to interact with supported metal components affecting the catalyst's properties and subsequently its catalytic performance. Therefore, H₂-TPR studies of M-TiO₂ catalysts can provide information on the interactions between the metal and TiO₂ support[33],

which can be correlated to its catalytic activity for methanol steam reforming reactions. **Fig. 8** shows a series of TPR profiles for different M-TiO₂ catalyst samples carried out under identical operating conditions, illustrating the reduction behavior of incorporated metal oxides. The TPR profile of TiO₂ (**Fig. 8a**) showed a broad low intensity peak in the temperature range of 410-630 °C, indicating the reduction of surface TiO₂ molecules. Other researchers have also found similar TiO₂ reduction behavior, with the observed reduction temperature varied between 400 and 720 °C [34-37].

Fig. 8. TPR profiles of different M-TiO₂ catalyst samples.

The TPR profile of 10%Pd-TiO₂ shown in **Fig. 8b** exhibited an interesting reduction behavior. The consumption of H₂ started at 50 °C and yielded an intense peak centered at 73 °C that corresponds to reduction of PdO on the surface to Pd⁰ [38, 39]. With further increase in temperature, four more peaks were observed: a sharp negative peak (81-108 °C), a wide positive peak (105-225 °C), a wide negative peak (225-383 °C) and a low intensity positive peak (383-460 °C). The positive peak centered at about 160 °C corresponds to the reduction of PdO particles located inside the porous structure which are more dispersed due to the comparatively

442 stronger interactions with TiO_2 support [10, 40, 41]. Both PdO reduction peaks were followed by
 443 negative peaks which can be attributed to the release of H_2 from the decomposition of the
 444 palladium hydride (PdH). The observed PdH decomposition at about 85 °C is in good agreement
 445 with earlier reports [40, 42]; however, the peak observed at higher temperature of about 300 °C
 446 was not reported before. We believe that Pd^0 formed at both stages of reduction undergoes the
 447 hydride formation which subsequently decomposed with increase in temperature resulting in
 448 negative peaks. Finally, the peak centered at 420 °C is assigned to the reduction of TiO_2 surface
 449 molecules. The observed decrease in the reduction temperature of TiO_2 from 530 °C to 420 °C in
 450 the presence of Pd is attributed to the interactions between Pd and TiO_2 which have also been
 451 observed for other noble metals [36, 43]. Shen et al. [38] suggested that the dissociation of
 452 hydrogen on the Pd particles and its successive spillover to TiO_2 leads to its lower temperature of
 453 reduction. These moderate to higher levels of interactions between Pd and TiO_2 surface could be
 454 responsible for the observed uniform dispersion of Pd in TiO_2 as shown in EDX studies
 455 (**Fig. 7d**). The TPR profile of 10% Cu- TiO_2 (**Fig. 8c**) showed two overlapping peaks of high
 456 intensity in the temperature range of 60-250 °C. They were followed by a wide and very low
 457 intensity peak spanned between 260 to 380 °C. Similar reduction behavior with coinciding peaks
 458 was also observed by other researchers [44, 45]. These peaks indicated the co-existence of three
 459 types of copper species in the calcined 10% Cu- TiO_2 sample. While the first two peaks centered
 460 at 153 °C and 175 °C were attributed to the reduction of bulk CuO species with comparatively
 461 insignificant but varying degree of interactions, the third peak suggested the reduction of bulk
 462 crystalline copper oxide that has moderate interactions with TiO_2 support [46-48]. The TPR profile
 463 also showed a very low intensity peak in the temperature range of 400-500 °C that can be
 464 attributed to the reduction of surface TiO_2 . Larsson et al. observed a significant decrease in the

reduction temperature of TiO_2 in the presence of CuO , suggesting an interaction between CuO and TiO_2 [49, 50]. Thus, the observation of very low peak intensity with a small shift in reduction temperature could be due to insignificant interactions between CuO and TiO_2 in the present study. This is consistent with the EDX mapping of Cu shown in **Fig.7a** where copper was seen to be poorly dispersed compared to the other metals.

The TPR profile of 10%Co- TiO_2 contained a broad area of H_2 consumption which started at 320 °C and continued to about 900 °C. The broad peak area apparently consisting of several overlapping reduction peaks can be de-convoluted into three peaks with first centered at 460 °C, second at 535 °C and last one at 720 °C. The overlapping behavior of first and second peak was in good agreement with other studies which were assigned to the stepwise reduction of Co_3O_4 to metallic Co ($\text{Co}^{3+} \rightleftharpoons \text{Co}^{2+} \rightleftharpoons \text{Co}^0$) [51-53]. By analogy to previous studies, the major peak observed at 720 °C can be attributed to the reduction of cobalt titanate (CoTiO_3) [54, 55]. However, it should be noted that although the behavior of the reduction was consistent with some of the earlier studies, the reduction peak positions in the present study are observed at comparatively higher temperature [56-59]. While Jalama et al. [57] observed the three analogous peaks at 344, 373 and 545 °C, Riva et al. found them in the range of 300 to 720 °C [56]. Thus, based on the TPR data and high dispersion of Co in the TiO_2 matrix observed in EDX analysis (**Fig.7b**) it can be inferred that very strong interactions exist between cobalt and TiO_2 support in the 10%Co- TiO_2 catalyst synthesized in this study using one-step method.

In contrast to the high temperature reduction behavior of Co- TiO_2 , complete reduction of 10%Ni- TiO_2 catalyst sample was achieved by 600 °C. The main sharp peak at 400 °C was followed by a low intensity wide shoulder peak centered at ~530 °C. While the first peak can be assigned to the reduction of NiO particles having moderate interaction with the TiO_2 surface, the

second peak is attributed to the reduction of NiO having moderate-to-stronger interactions with TiO₂[14, 60]. In general, the reduction of bulk NiO particles in the absence of interactions with the support occurs in the temperature range of 280-300 °C [61, 62]. The nonexistence of this peak indicates that the present 10% Ni-TiO₂ catalyst prepared by one-pot synthesis method does not contain such bulk NiO particles. Furthermore, H₂ consumption peaks for the reduction of NiTiO₃, which are generally observed above 600 °C are not present suggesting the absence of very strong NiO-TiO₂ interactions [60, 63]. Yan et al. [60] claimed that both these bulk NiO and NiTiO₃ are catalytically inactive and interestingly they are not present in our 10% Ni-TiO₂ catalyst. The observed moderate interactions between Ni and TiO₂ were also evident in the reasonable dispersion of Ni shown in **Fig. 7c** of EDX studies.

The H₂ consumption profile as a function of temperature for 10% Zn-TiO₂ catalyst sample is presented in **Fig. 8f**. The TPR profile shows one clear symmetric peak at about 430 °C and two overlapping peaks centered at about 650 °C and 750 °C. It is interesting to note that a significant portion of ZnO in TiO₂ was reduced well below the generally reported bulk ZnO reduction temperature of about 650 °C [64, 65]. This clearly indicates the existence of the strong-metal support interactions between Zn and TiO₂ promoting the reduction of ZnO. The presence of reduction peak at 750 °C can be attributed to the very strong metal-support interaction leading to the formation of Zn-titanate spinel structures. Finally, the TPR profile for 10% Sn-TiO₂ (**Fig. 8g**) shows three distinct overlapping reduction peaks in the temperature range of 150-800 °C. Nava et al. [66] and Corradini et al. [67] also reported similar three stage reduction behavior for Sn/TiO₂. The H₂ consumption peak at 320 °C is assigned to the reduction of SnO₂ species which are strongly interacting with the TiO₂ surface. The two other peaks centered at 500 °C and 650 °C are attributed to the two step reduction of bulk SnO₂ to metallic Sn ($\text{Sn}^{4+} \rightarrow \text{Sn}^{2+} \rightarrow \text{Sn}^0$).

[68].As the reported temperature for bulk SnO₂reduction is generally above 750 °C [69], the observed lower reduction temperature of bulk SnO₂ in the present study shows the existence of varied degree of interactions between the Snparticles and TiO₂.

3.8. Performance test of M-TiO₂ for SRM

To gain further insights in to the metal-support interactions, the comparative performance of different metal componentsincluding Cu, Co, Ni, Pd, Zn and Sn incorporated in mesoporous TiO₂ support was investigated for H₂ production.**Fig. 9**illustrates the catalytic behavior of each catalyst for SRM showing the effect of reaction temperature on methanol conversion and selectivity towards different products, namely, H₂, CO, CO₂ and CH₄. One common trend observed was the increase in methanol conversion with increase in reaction temperature for all catalysts showing a strong influence of temperature on the catalysts' activity. For example, for 10%Pd-TiO₂ catalyst, methanol conversion increased from 8% to about 98 % with increase in temperature from 150 °C to 350 °C. This can obviously be attributed to the endothermic nature of steam reforming reaction (**Eq.(5)**).

Fig. 9. The effect of reaction temperature on: (a) methanol conversion (b) H₂ selectivity (c) CH₄ selectivity (d) CO selectivity (e) CO₂ selectivity for different M-TiO₂ catalysts

The conspicuous outcome of these results (**Fig. 9**) is the remarkable differences in the SRM activity and selectivity among the different metal components incorporated in TiO₂. The methanol conversion vs temperature profiles in **Fig. 9a** reveal that while Pd/TiO₂ catalyst is the most active, Sn/TiO₂ is the least active for SRM reaction establishing an overall activity trend of Pd > Ni > Zn > Co >> Cu >> Sn. This activity sequence of M-TiO₂ can be linked to the

specific interactions observed between the metal component and the TiO₂ support (TPR section, above). The ease of PdO reduction and moderate to stronger interactions between Pd and TiO₂ resulting in higher dispersion could be responsible for its observed highest activity. In contrast, very strong metal-support interactions observed in 10%Co-TiO₂ led to high dispersion of Co, the consequential high temperature reduction could be responsible for its lower SRM activity. For both Ni and Zn where the specific metal-support interactions led to lower reduction temperature compared to their bulk counterparts, reasonable SRM activity next to Pd was observed. For example, at 350 °C, 10%Ni-TiO₂ and 10%Zn-TiO₂ yielded about 86% and 82% methanol conversion, respectively. The significantly lower activity of 10%Cu-TiO₂ catalyst could be ascribed to the absence of noticeable metal-support interactions resulting in lower dispersion and sintering. In contrast, in our very recent study [70], Cu-MCM-41 showed excellent activity and selectivity for SRM. Given the inert nature of silica support reducing or eliminating the possible metal-support interactions, the outstanding performance of Cu-MCM-41 was attributed to highly uniform dispersion of Cu in very high surface area MCM-41 support. The results for Ni-TiO₂ and Cu-TiO₂ catalysts in this study are similar to that observed for ethanol steam reforming activity of Ni/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ catalysts reported by Aupretre et al. [71]. However, in their studies, Zn/ γ -Al₂O₃ showed significantly lower activity compared to Ni/ γ -Al₂O₃. The higher SRM activity of Zn-TiO₂ which was comparable to that of Ni-TiO₂ in the present study supports our hypothesis that the specific interactions between Zn and TiO₂ observed in TPR analysis are responsible for its promising SRM activity. Interestingly, even though moderate level of interactions were observed between Sn and TiO₂ resulting in a portion of SnO₂ reduction at lower temperature, it showed an insignificant activity for SRM reaction with just 10% conversion at 350 °C. These results further suggest that for favorable steam reforming activity, there need to

exist optimum interactions between support and metal components which are again characteristics of the particular metal-support system.

While methanol conversion varied significantly for different M-TiO₂ catalysts, all of them showed more than 90% H₂ selectivity except for Sn-TiO₂, where the selectivity dropped to less than 50% due to excessive methanation reaction (**Eq.(8)**) as shown in **Fig. 9**. It was observed that although both Ni-TiO₂ and Pd-TiO₂ exhibited very good activity for decomposition reaction leading to higher methanol conversions (**Eq.(6)**), the activity for water-gas-shift reaction (**Eq.(7)**) was almost insignificant resulting in very high (>80% for Ni and >70% for Pd at 350) CO selectivities over the range of reaction temperature shown in **Fig. 9d**. The selectivity of CO was also observed to depend on the relative activity for the water-gas-shift reaction (**Eq.(7)**) and methanation reaction (**Eq.(8)**). Although methanation reaction does help in decreasing CO selectivity, one mole CH₄ formation results in loss of 3 moles of product H₂. For example, comparatively lower CO selectivity observed for Co-TiO₂, Cu-TiO₂ and Sn-TiO₂ were attributed to the formation of methane at the expense of decreased H₂ selectivity. On the other hand, Zn-TiO₂ showed the best performance among the studied catalysts both in terms of desired higher activity for water-gas-shift and lower activity for methanation reaction. Based on the important criterion of lower CO selectivity, the different metals followed the order: Zn-TiO₂ < Sn-TiO₂ < Co-TiO₂ < Cu-TiO₂ < Pd-TiO₂ < Ni-TiO₂.

As Zn-TiO₂ catalyst exhibited lowest CO selectivity among different metals studied, Zn loading was varied from 5-20% to investigate further the effect of Zn loading on SRM activity and selectivity. The results of these SRM studies are presented in **Fig. 10**. It was interesting to note that the SRM activity increased with increase in loading up to 15% and then decreased with further increase in Zn loading. For example, at 300 °C reaction temperature, the conversion

increased from 28% to 66% with increase in Zn loading from 5% to 10%. It remained almost constant at 15% loading giving slightly higher conversion of ~68%. However, further increase in Zn loading to 20% drastically decreased methanol conversion to only about 19%.

Fig. 10. The effect of reaction temperature on methanol conversion and product selectivity for (a) 5%Zn-TiO₂ (b) 10%Zn-TiO₂ (c) 15%Zn-TiO₂ and (d) 20%Zn-TiO₂ catalysts.

This behavior is consistent with observed variations in surface area of Zn-TiO₂ catalyst with changes in Zn loading (**Table 1**). The surface area of Zn-TiO₂ catalyst was also observed to increase with increase in Zn loading from 5 to 15% and then decreased drastically at 20% Zn loading. Thus, the observed change in the SRM activity with Zn loading can be attributed to its influence on the catalyst surface area. The observed methanol conversion and CO selectivity values indicate that the 15%Zn-TiO₂ is the most favorable catalyst among the different catalysts investigated in the present investigation.

4. Conclusions

A simple one-step procedure was used to synthesize different mesoporous M-TiO₂ (M: Cu, Co, Ni, Pd, Sn, and Zn) catalysts for investigating the specific metal-TiO₂ interactions and their influence on SRM activity and selectivity. Synthesized M-TiO₂ catalysts showed significantly high surface areas in the range of 99-309 m²/g depending on the type of incorporated metal species. TGA-DSC and XRD studies revealed that incorporation of metal ions significantly delayed the TiO₂ crystallization which can be attributed to the decreased mobility of Ti ions caused by metal atoms acting as impurity or adatoms. This delayed crystallization led to the formation of M-TiO₂ catalysts with significantly higher surface areas compared to TiO₂ itself. Both the type of metal and loading significantly influenced the textural properties of prepared catalysts. The results from SRM studies indicated the remarkable differences in catalytic performances of different M-TiO₂ catalysts due to specific metal-support interactions controlling the reducibility and dispersion of metal particles in TiO₂ matrix. While the SRM activity for different M-TiO₂ catalysts followed the sequence of Pd-TiO₂ > Ni-TiO₂ > Zn-TiO₂ > Co-TiO₂ > Cu-TiO₂ > Sn-TiO₂, the lower CO selectivity was observed in the order of Zn-TiO₂ < Sn-TiO₂ < Co-TiO₂ < Cu-TiO₂ < Pd-TiO₂ < Ni-TiO₂. Furthermore, the SRM activity of Zn-TiO₂ catalysts was observed to increase with increase in Zn loading from 5 to 15% and then decreased with further increase in Zn loading to 20%. The observed optima for Zn-TiO₂ catalyst with variation in Zn loading was attributed to its substantial influence on the textural properties. Among the different catalysts investigated in the present study, 15% Zn-TiO₂ showed best SRM performance with 88% methanol conversion, ~100% H₂ selectivity and 1.3% CO selectivity at 350 °C reaction temperature.

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Catalyst	Surface Area (m ² /g)	Pore Size (nm)	Pore Volume (cm ³ /g)	Actual Metal Loading (wt %) ICP-OES	TiO ₂ Crystal Size (nm)	Metal Crystal Size (nm)
TiO₂	146.6	3.59	0.172	0	17.18	-
10Cu-TiO₂	285.6	3.28	0.190	10.6	9.84	20.9
10Ni-TiO₂	309.8	3.32	0.203	13.9	-	-
10Co-TiO₂	215.1	3.30	0.142	13.3	4.03	-
10Sn-TiO₂	164.3	3.29	0.134	5.26	7.52	-
10Pd-TiO₂	99.7	3.32	0.081	5.32	8.78	49.4
10Zn-TiO₂	250.2	3.31	0.158	12.52	6.79	-
5Zn-TiO₂	178.8	3.31	0.132	5.2	7.29	-
15Zn-TiO₂	257.5	3.29	0.175	15.14	-	-
20Zn-TiO₂	140.1	3.30	0.113	17.18	-	-

Table 1: Textural properties, actual metal loading and crystallite sizes of different M-TiO₂ catalyst samples