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# Ni–Sr/TiZr for H<sub>2</sub> from methane *via* POM: Sr loading & optimization†

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Achieving remarkable H<sub>2</sub> yield with significantly high H<sub>2</sub>/CO over Ni-based catalysts through partial oxidation of methane (POM) is a realistic approach to depleting the concentration of CH<sub>4</sub> and using H<sub>2</sub> and CO as synthetic feedstock. This study examined Ni catalysts on titania–zirconia for methane conversion *via* POM at 600 °C and atmospheric pressure. The addition of strontium to the catalyst was explored to improve its performance. Catalysts were characterized by X-ray diffraction, Raman-infrared-UV-vis spectroscopy, and Temperature-programmed reduction-desorption techniques (TPR, TPD). 2.5 wt% Sr addition induced the formation of the highest concentration of extreme basic sites. Interestingly, over the unpromoted catalyst, active sites are majorly generated by hardly reducible NiO species whereas upon 2.5 wt% promoted Sr promotional addition, most of active sites are derived by easily reducible NiO species. 45% CH<sub>4</sub> conversion and 47% H<sub>2</sub> yield with H<sub>2</sub>/CO = 3.5 were achieved over 2.5 wt% Sr promoted 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst. These results provide insight into the role of basic sites in enhancing activity through switching indirect pathways over direct pathways for POM. Further process optimization was carried out in the range of 10 000–22 000 SV, 0.35–0.75 O<sub>2</sub>/CH<sub>4</sub> and 600–800 °C reaction temperature over 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> by using central composite design under response surface methodology. The optimum activity as high as ~88% CH<sub>4</sub> conversion, 86–87% yield of H<sub>2</sub>, and 2.92H<sub>2</sub>/CO were predicted and experimentally validated at 800 °C reaction temperature, 0.35O<sub>2</sub>/CH<sub>4</sub> ratio, and 10 000 space velocity.

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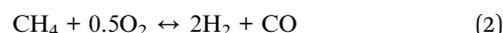
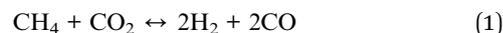
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## 1. Introduction

In the current global warming scenario, mitigation of greenhouse gases is urgently needed to save the ecosystem on Earth. Among the greenhouse gases, methane is 25 times more potent than CO<sub>2</sub>.<sup>1</sup> Catalyst communities across the globe are trying to develop a proper catalytic route for the conversion of CH<sub>4</sub>. The catalytic direct decomposition of CH<sub>4</sub> into C and H<sub>2</sub> is struggling due to massive carbon decomposition and quick

deactivation. Oxidant-assisted oxidation of CH<sub>4</sub> also gives way to continuous oxidation of carbon deposits into the syngas (H<sub>2</sub> and CO). In dry reforming of methane (DRM), CO<sub>2</sub> is the oxidant; in the steam reforming of methane (SRM), H<sub>2</sub>O is the oxidant; and in partial oxidation of methane, O<sub>2</sub> is the oxidant for CH<sub>4</sub> oxidation (eqn (1)–(3)). The typical stoichiometric H<sub>2</sub>/CO ratio in DRM, POM, and SRM is 1, 2, and 3, respectively.



According to the stoichiometry of the POM reaction, the H<sub>2</sub>/CO ratio over the POM reaction should be equal to 2. But recently, >3H<sub>2</sub>/CO ratio during POM reaction has drawn marked attention.<sup>2,3</sup> It indicates the presence of indirect reaction pathways along with the direct POM pathway (Fig. 1) The indirect reaction pathway of POM can be summarized as the total oxidation of CH<sub>4</sub> into “CO<sub>2</sub> and H<sub>2</sub>O” (Fig. 1, step 1) followed by the involvement of “CO<sub>2</sub> and H<sub>2</sub>O” into the oxidation of CH<sub>4</sub> through DRM (Fig. 1, step 2a) and SRM reaction (Fig. 1, step 2b)

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respectively. The total oxidation of  $\text{CH}_4$  is catalysed by  $\text{NiO}$ , whereas POM, DRM, and SRM are catalysed by metallic  $\text{Ni}$ .<sup>4</sup> Overall, the direct and indirect pathways of POM decide the final production distribution.

$\text{CH}_4$  and  $\text{O}_2$  undergo control oxidation over  $\text{B}_2\text{O}_3$ -based catalysts and form formate species which is not dissociated further.<sup>5</sup> Ru dispersed over  $\text{Al}_2\text{O}_3$  ( $\text{Ru}/\text{Al}_2\text{O}_3$ ) carried out the complete oxidation of  $\text{CH}_4$  and  $\text{O}_2$  into syngas. However, adding Re to  $\text{Ru}/\text{Al}_2\text{O}_3$  catalyses  $\text{CH}_4$  and  $\text{O}_2$  to control oxidation into formate species, which dissociates into syngas.<sup>6</sup> Combining noble metals like Rh, Ru, or Pd with a less expensive metal like nickel creates highly effective catalysts for (POM) reactions. Still, the usual high cost of catalysts is a significant limitation in practical applications.<sup>6–8</sup> Selecting proper supports and promoters for Ni-based catalysts may be as efficient as noble metal-based catalysts. Ni supported over lanтана and Ni supported over titania have little life span due to the oxidation of active sites Ni by support lanтана or titania.<sup>9–11</sup> The partial coverage of active sites by diffusion of  $\text{TiO}_2$  and partial phase transformation of titania phase were also reported.<sup>12</sup> The alumina support may be a suitable carrier for Ni catalysts, but the acidic nature of alumina may be less interactive with acidic  $\text{CO}_2$  gas. So, one route of POM's indirect pathway (step 2a) may be affected. If we select essential support like  $\text{MgO}$  for the dispersion of Ni, The  $\text{Ni}/\text{MgO}$  catalyst was found to be more prompt to total oxidation of methane than partial oxidation.<sup>9</sup> Ni has less dispersion over silica than zirconia.<sup>13</sup> Even  $\text{ZrO}_2$  and yttria-stabilized- $\text{ZrO}_2$  efficiently carry out POM reactions.<sup>14</sup> Over yttria-stabilized- $\text{ZrO}_2$ , both  $\text{CH}_4$  and  $\text{O}_2$  undergo control oxidation and form formate species, which further break down into syngas. That means it favours the direct methanation route. Again, Ni-supported over  $\text{ZrO}_2$  has a higher  $\text{H}_2$  uptake than Ni-supported over  $\text{CeO}_2$ .<sup>10</sup> The support  $\text{ZrO}_2$  has phase transition issues at high temperatures, and Ni-supported over  $\text{ZrO}_2$  may be seriously affected by metal sintering. Overall,  $\text{ZrO}_2$  and  $\text{TiO}_2$  support have excellent redox properties. Their mobile lattice

oxygen is easily accessible in an oxidation reaction, which can minimize the time delay in oxygen transport in POM reaction. However, individually, both have a severe phase transition, and titania has excessive diffusion and active sites' oxidation issues. We have recently developed titania-modified  $\text{ZrO}_2$  support, and the new hybrid support has eliminated all the challenges of phase transition, excessive diffusion, and over-oxidation.<sup>15</sup> When different types of promoters (Ce, Cs, and Sr) were added, Ni distributed over titania-modified zirconia ( $\text{Ni}/\text{TiZr}$ ) continually maintained an  $\text{H}_2/\text{CO}$  ratio of  $>3$  for 300 minutes on stream.<sup>3</sup> Sr addition over  $\text{Ni}/\text{TiZr}$  caused the highest activity due to the maximum concentration of active sites and the higher edge of reducibility. Cs addition over  $\text{Ni}/\text{TiZr}$  resulted in inferior catalytic activity due to the lowest density of basic sites. The enhanced reducibility was also observed upon the promotional addition of Sr over  $\text{Ni}/\text{ZrO}_2\text{-Al}_2\text{O}_3$  catalyst.<sup>16</sup> The addition of Sr increases the basicity of the surface, which interacts with more acidic gases like  $\text{CO}_2$  in the indirect POM pathway and helps in the activation of  $\text{CO}_2$ . Further, a large size of Sr can stabilize  $\text{CO}_2$  over the catalyst surface as a bidentate carbonate intermediate, as well as enhance the dissociation of C–H by surface oxygen species.<sup>17</sup>  $\text{Sr}^{+2}$ -mediated  $\text{CO}_2$  was found to be a better oxidizing agent, inhibiting the deposition of carbyne-type carbon.<sup>15</sup> So, it is necessary to extend the research on the different loadings of Sr promoters over Ni/titania-zirconia catalysts toward POM. After proper catalyst selection, the next step is to set reaction conditions/experimental factors (like temperature,  $\text{O}_2/\text{CH}_4$  ratio, and space velocity) to get maximum  $\text{H}_2$  yield with a high  $\text{H}_2/\text{CO}$  ratio. Performing fresh reactions after varying reaction conditions in order to optimize activity needs much time, workforce, and expenditure. With the help of statistical tools like response surface methodology (RSM), the optimum activity can be predicted with a very high level of accuracy by few experimental data. The activity is collected as the response of a mathematical equation that considers all the experimental factors and their interactions.<sup>18</sup> In dry reforming reaction, central composite design and Box–Behnken design under RSM are investigated where predicted values and experiment values are found very close to each other.<sup>19–23</sup> However, for POM reactions, such statistical investigations are less considered and need to be explored by the catalytic community.

Herein, titania modified- $\text{ZrO}_2$  is investigated for supporting catalytic active site “5 wt% Ni” and promoter “1–3 wt% Sr” in the target of limiting phase transition of  $\text{ZrO}_2$  and restricting the diffusion for “ $\text{TiO}_2$ ” and stabilizing the  $\text{CO}_2$  intermediate in favor of POM reaction. The catalysts are characterized by surface area-porosity measurement, X-ray diffraction, Raman, infrared, ultraviolet-visible spectroscopy,  $\text{H}_2$ -temperature-programmed reduction, and  $\text{O}_2$ -temperature-programmed oxide experiments, and  $\text{CO}_2$ -temperature programmed desorption. The thorough characterization and catalytic activity reveal the role of Sr promoter for inducing phase stability and edge and strength of reducibility-basicity of  $5\text{Ni}/30\text{TiO}_2 + \text{ZrO}_2$  catalyst in the favour of POM reaction. The best catalyst is further investigated in process optimization by using a central composite design under response surface methodology in the range of 10 000–22 000 SV, 0.35–0.75  $\text{O}_2/\text{CH}_4$ , and 600–800 °C reaction temperature.

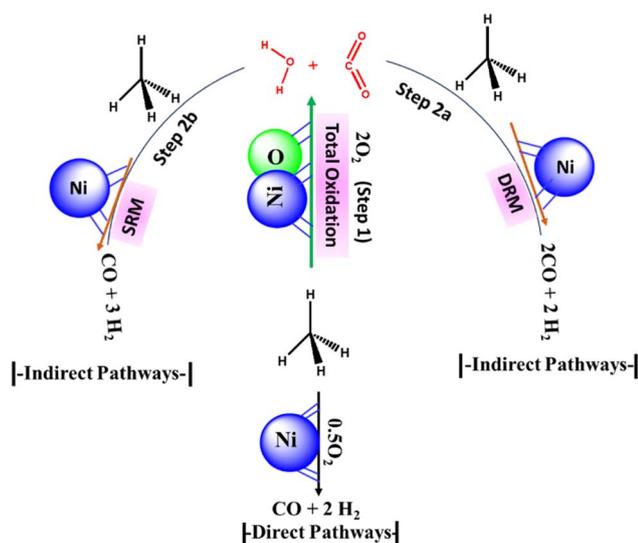


Fig. 1 The reaction scheme for POM (A) direct pathways (B) indirect pathways.



## 2. Experimental

### 2.1 Materials

Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (purity 98%, Alfa Aesar), Sr(NO<sub>3</sub>)<sub>2</sub> (Aldrich), 30 wt% TiO<sub>2</sub>-70 wt% ZrO<sub>2</sub> (Daiichi Kigenso Kagaku Kogyo Co). As per the specification of 30 wt% TiO<sub>2</sub>-70 wt% ZrO<sub>2</sub> (from Daiichi Kigenso Kagaku Kogyo Co., Ltd), it has a tetragonal-ZrO<sub>2</sub> phase and diffuse anatase-TiO<sub>2</sub> phase. The surface area of the 30 wt% TiO<sub>2</sub>-70 wt% ZrO<sub>2</sub> is 124 m<sup>2</sup> g<sup>-1</sup>, and 50% of the particles in the catalyst are smaller than 8.6 nm (*D*<sub>50</sub> = 8.6 nm).

### 2.2 Catalyst preparation

5 wt% equivalent of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous solution and 1–3 wt% equivalent of Sr(NO<sub>3</sub>)<sub>2</sub> solution nitrate aqueous solution is added over 30 wt.% TiO<sub>2</sub>-70 wt% ZrO<sub>2</sub> under stirring at 80 °C temperature. Stirring continues until the solution evaporates and the mixture turns into a paste. The solution was dried at 110 °C for 24 hours and then calcined at 600 °C for three hours. The catalyst is abbreviated as Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> (*x* = 1, 2, 2.5, 3 wt%).

### 2.3 Catalyst characterization

The BET surface area Powder X-ray diffraction (XRD) analysis of fresh catalyst was conducted by Rigaku (Miniflex) diffractometer using Cu K<sub>α1</sub> radiation ( $\lambda = 0.15406$  nm) operated at 40 mA and 40 kV. The N<sub>2</sub> adsorption-desorption and porosity results were obtained using a Micromeritics Tristar II 3020 surface area analyzer. 0.2–0.3 g of catalyst was degassed, and all samples were degassed before analysis using the Barrett, Joyner & Halenda (BJH) method. Temperature-programmed hydrogen reduction (H<sub>2</sub>-TPR) and temperature-programmed carbon dioxide desorption (CO<sub>2</sub>-TPD) measurements were performed on a chemisorption device (Micromeritics AutoChem II) by using a thermal conductivity detector over 70 mg catalyst sample, respectively. In H<sub>2</sub>-TPR, H<sub>2</sub> absorption is monitored up to 1000 °C under 10% H<sub>2</sub>/He gas, whereas in CO<sub>2</sub>-TPD, CO<sub>2</sub> desorption is monitored upon raising the temperature to 800 °C under 10% CO<sub>2</sub>/He gas. The transmission electron microscopy was conducted at 200 kV using an aberration-corrected JEM-ARM200F (JEOL) with a CEOS corrector. The spent catalyst sample underwent Raman analysis within the 1250–3000 cm<sup>-1</sup> range using a Laser Raman Spectrometer (JASCO, Japan) with a 532 nm beam excitation and 1.6 mW laser intensity. The exposure time was set to 10 seconds with 3 accumulations.

### 2.4 Catalyst activity test

The partial oxidation of methane was carried out over a 0.1 g catalyst in a tubular stainless-steel fixed bed reactor (PID Eng. & Tech, 9 mm I.D.). The temperature for the catalytic reaction was provided by the cylindrical furnace circumference of the catalyst bed. The temperature at the catalyst bed was monitored by an axially fixed K-type thermocouple in the catalyst bed. In the target of creating active sites before partial oxidation of methane, a reductive pretreatment of the catalyst was carried out under hydrogen (flow rate 30 mL min<sup>-1</sup>) for 1 h at 800 °C. Further, to

remove the hydrogen gas from the catalyst bed, the reactor was purged with N<sub>2</sub>. Then, the temperature of the reactor was stabilized at 600 °C for the POM reaction. The reaction gas mixture which consisted of 50% CH<sub>4</sub>, 25% O<sub>2</sub>, and 25% N<sub>2</sub> gases was allowed to pass through the fixed catalyst bed with the total flow maintained at 24 mL min<sup>-1</sup> and 14 400 mLg<sup>-1</sup> h<sup>-1</sup> space velocity. The products were analysed by a gas chromatograph equipped with a propak Q column, molecular sieve columns, and a thermal conductivity detector. The composition of effluent gases was calculated by the normalization method, and the equations for the determination of CH<sub>4</sub> conversion, CO<sub>2</sub> conversion, H<sub>2</sub> yield, CO yield, and H<sub>2</sub>/CO ratio are used as follows:

$$\text{CH}_4 \text{ conversion (\%)} = \frac{\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}}{\text{CH}_{4,\text{in}}} \times 100 \quad (4)$$

$$\text{CO}_2 \text{ yield (\%)} = \frac{\text{mol of CO}_2 \text{ in products}}{\text{mol of CH}_4 \text{ in feed}} \times 100 \quad (5)$$

$$\text{H}_2 \text{ yield (\%)} = \frac{\text{H}_{2,\text{out}}}{2 \times \text{CH}_{4,\text{in}}} \times 100 \quad (6)$$

$$\text{CO yield (\%)} = \frac{\text{mole of CO in product}}{\text{mol of CH}_{4,\text{out}} + \text{mol of O}_{2,\text{in}}} \times 100 \quad (7)$$

$$\frac{\text{H}_2}{\text{CO}} = \frac{\text{mole of H}_2 \text{ produced}}{\text{mole of CO produced}} \quad (8)$$

## 3. Result and discussion

### 3.1 N<sub>2</sub> physisorption

The N<sub>2</sub> adsorption isotherm and surface parameters (surface area, pore volume, and pore diameter) of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> (*x* = 1, 2, 2.5, 3) catalysts are shown in Fig. 2 and Table 1. The adsorption-desorption profile of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> (*x* = 1, 2, 2.5, 3) catalysts are characterized by type IV adsorption with H1 hysteresis loop which indicates the presence of mesoporous domains of the cylindrical architect.<sup>24,25</sup> For such isotherm, a desorption branch is recommended for pore size analysis,<sup>26</sup> and the “dV/dlog(*w*)” vs. “*w*” (“*w*” is pore width) plot shows pore size distribution. The 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> has a maximum surface area (124 m<sup>2</sup> g<sup>-1</sup>), pore volume (0.36 cm<sup>3</sup> g<sup>-1</sup>), and an average 8.6 nm pore diameter. The catalyst has a bimodal distribution of pore size in the range of 7.0 nm and 10.2 nm. Interestingly, upon promotional addition of Sr over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>, the pore size distribution becomes narrower and monomodal in the 6.3–6.8 nm range. The pore volume remains almost intact upon the addition of Sr promoters over the 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst. Upon adding 1–2 wt% Sr loading over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>, the surface area of the catalyst is decreased marginally. The 5Ni<sub>2</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst has a minimum surface area (119 m<sup>2</sup> g<sup>-1</sup>) but a maximum pore diameter of 8.6 nm among the promoted samples.

### 3.2 X-ray diffraction

The X-ray diffraction study of fresh and spent 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> (*x* = 1–3 wt%) catalysts are shown in



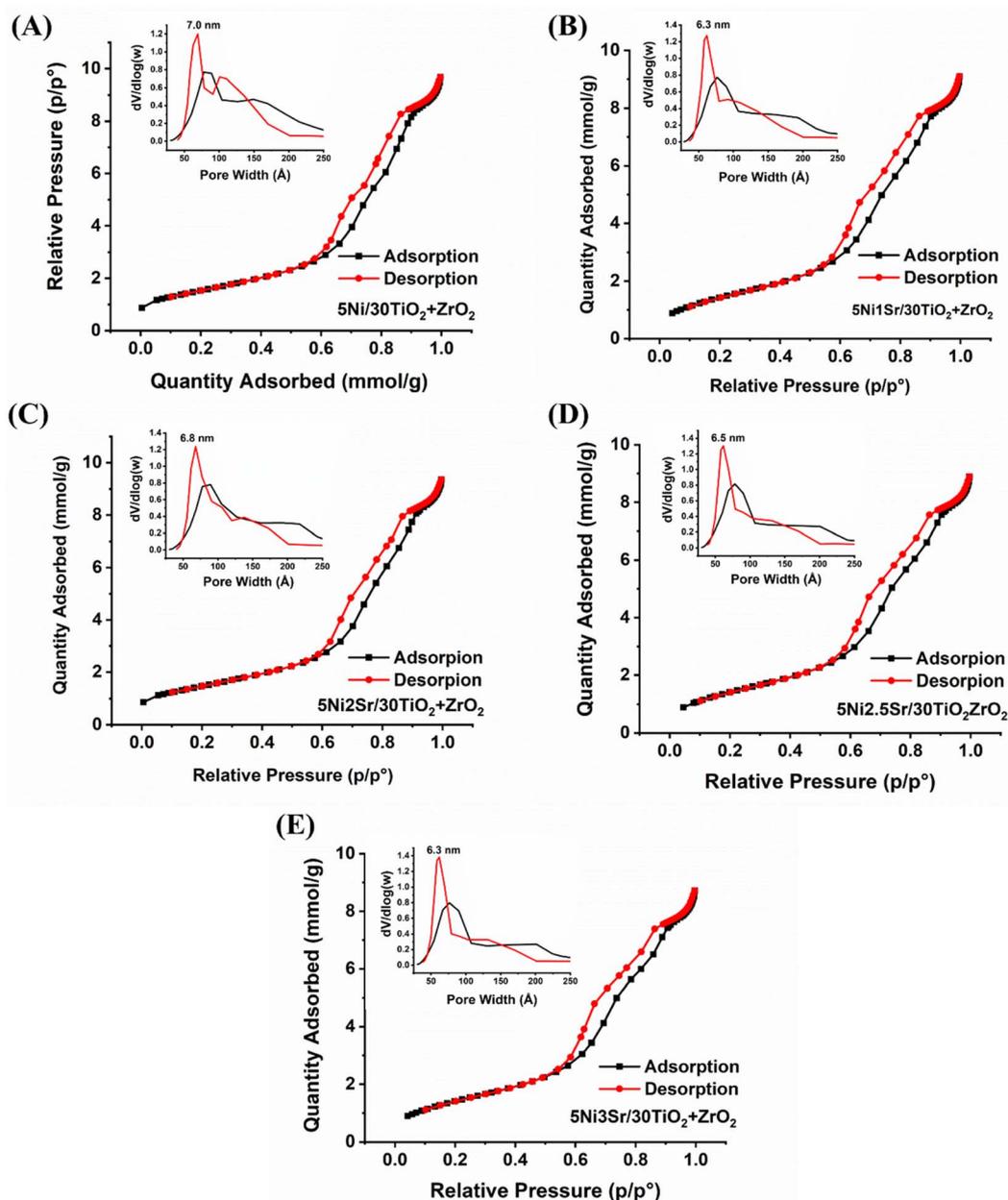


Fig. 2  $N_2$  adsorption isotherm and porosity distribution (inset figure) of  $5Ni/30TiO_2 + ZrO_2$  and  $5Ni_xSr/30TiO_2 + ZrO_2$  ( $x = 1-3$  wt%) catalysts.

Table 1 Surface area, pore volume, and average pore size of  $5Ni/30TiO_2 + ZrO_2$  and  $5Ni_xSr/30TiO_2 + ZrO_2$  ( $x = 1-3$  wt%) catalysts

Catalyst	Surface area ( $m^2 g^{-1}$ )	Pore volume ( $cm^3 g^{-1}$ )	Average pore diameter (nm)
$5Ni/30TiO_2 + ZrO_2$	124	0.36	8.6
$5Ni1Sr/30TiO_2 + ZrO_2$	123	0.36	7.8
$5Ni2Sr/30TiO_2 + ZrO_2$	119	0.37	8.6
$5Ni2.5Sr/30TiO_2 + ZrO_2$	122	0.36	7.8
$5Ni3Sr/30TiO_2 + ZrO_2$	121	0.35	7.6

Fig. 3. Fresh  $5Ni/30TiO_2 + ZrO_2$  catalyst has intense tetragonal  $ZrO_2$  phase (at Bragg's angle  $2\theta = 30.28^\circ, 35.15^\circ, 43.05^\circ, 50.50^\circ, 53.60^\circ, 60.32^\circ, 62.76^\circ$ ; JCPDS reference number 01-079-1771) and diffuse peaks for Rutile  $TiO_2$  phase (at Bragg's angle  $2\theta =$

$27.51^\circ, 35.15^\circ, 53.60^\circ$ ; JCPDS reference number 00-034-0180), anatase  $TiO_2$  phase (at Bragg's angle  $2\theta = 25.28^\circ, 47.76^\circ, 53.60^\circ, 63.77^\circ$ ; JCPDS reference number 01-071-1168) and cubic  $NiO$  phase (at Bragg's angle  $2\theta = 43.20^\circ$ ; JCPDS reference number



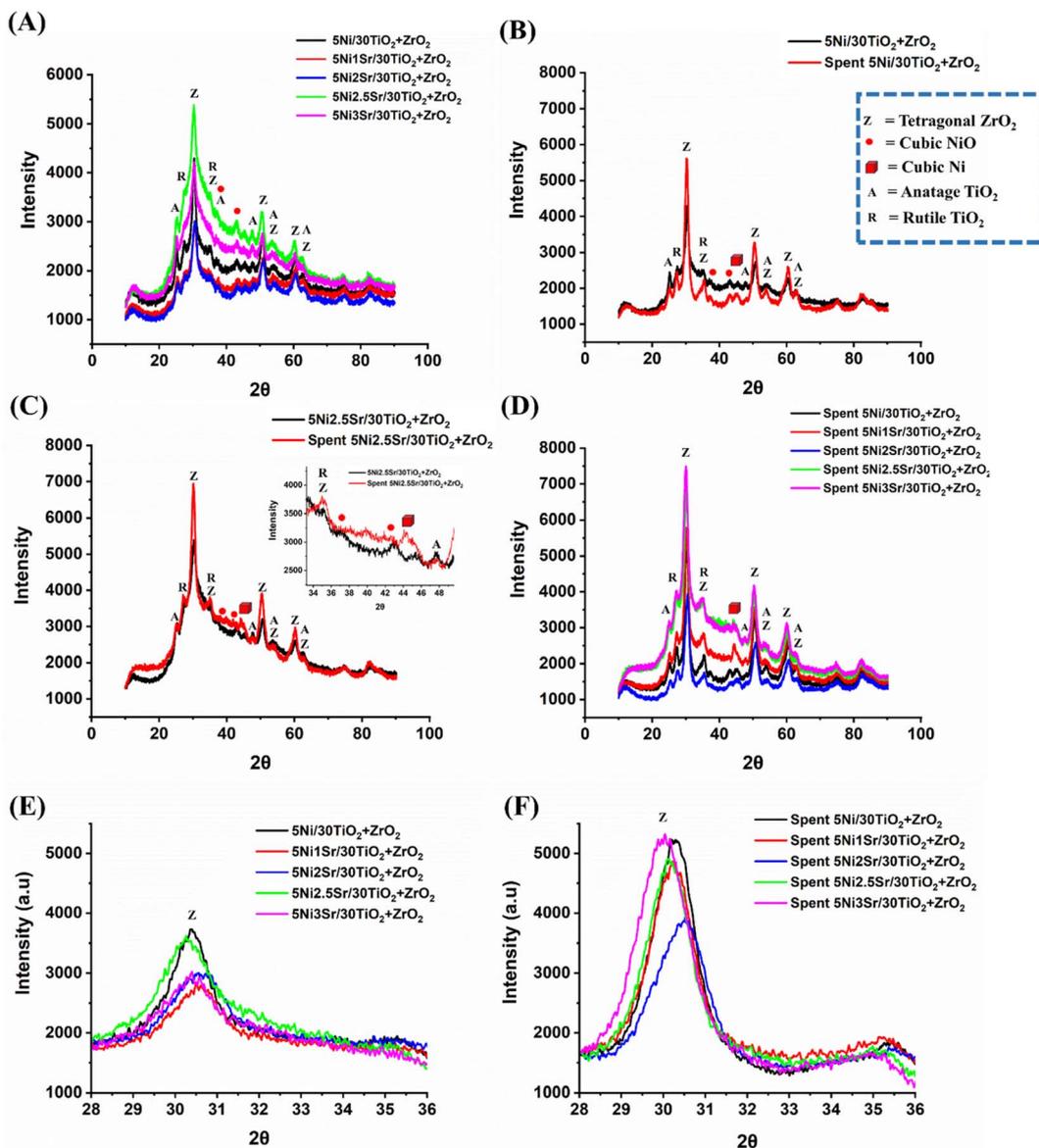


Fig. 3 (A) Fresh XRD of all catalysts, (B) fresh-spent XRD of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>, (C) fresh-spent XRD of 5Ni<sub>2.5</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub>, (D) spent XRD of all catalysts, (E) fresh XRD peak of ZrO<sub>2</sub> about 30.5° Bragg's angle (F), spent XRD peak of ZrO<sub>2</sub> about 30.5° Bragg's angle.

00-047-1049). The crystalline phases for promoter oxides are not observed over Sr-promoted catalysts, which indicates the fine dispersion of promoter oxide. The X-ray diffraction intensity for ZrO<sub>2</sub> and TiO<sub>2</sub> phases is found to be a maximum of over 2.5 wt% Sr promoted 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst compared to other catalysts. The loading above 2.5 wt% Sr over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> results in a fall of crystallinity of ZrO<sub>2</sub> and TiO<sub>2</sub> phases. Over-spent catalysts, the diffraction pattern for metallic cubic Ni (44.68°; JCPDS reference number 00-004-0850) appears, and the peak intensity of tetragonal ZrO<sub>2</sub>, Rutile TiO<sub>2</sub> and Anatase TiO<sub>2</sub> phases are intensified. During the POM reaction, the crystalline peak intensity of tetragonal ZrO<sub>2</sub> is grown slowest over 2 wt% Sr promoted 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> than the rest of the catalyst (Fig. 3E and F). It indicates the role of the promoter on support's crystallinity during the POM reaction.

### 3.3 Raman, infrared and ultra-violet spectra

The Raman spectra of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> ( $x = 1, 2, 2.5, 3$ ) catalyst are shown in Fig. 4A. The Raman band at 395 cm<sup>-1</sup> (B<sub>1g</sub>), 517 cm<sup>-1</sup> (A<sub>1g</sub>, B<sub>1g</sub>), 642 cm<sup>-1</sup> (E<sub>g</sub>) are observed for anatase TiO<sub>2</sub> phases whereas the Raman band at 834 cm<sup>-1</sup> (B<sub>2g</sub>) signifies for rutile phase.<sup>27,28</sup> The intensity of the anatase phase is higher than the rutile phase over titania-zirconia-supported Ni catalyst. Previously, it was reported that incorporating zirconia atom into titania lattice stabilized the anatase phase.<sup>27,29</sup> The Raman band at 283 cm<sup>-1</sup> and 642 cm<sup>-1</sup> may be associated with partially tetragonal zirconia and partially by segregated TiO<sub>2</sub> phases, or it may be related to (ZrTi)O<sub>x</sub> material. Sr addition over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst is found to induce the Raman vibration pattern incredibly. Upon addition of just 1 wt% Sr over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>, the E<sub>g</sub> vibration



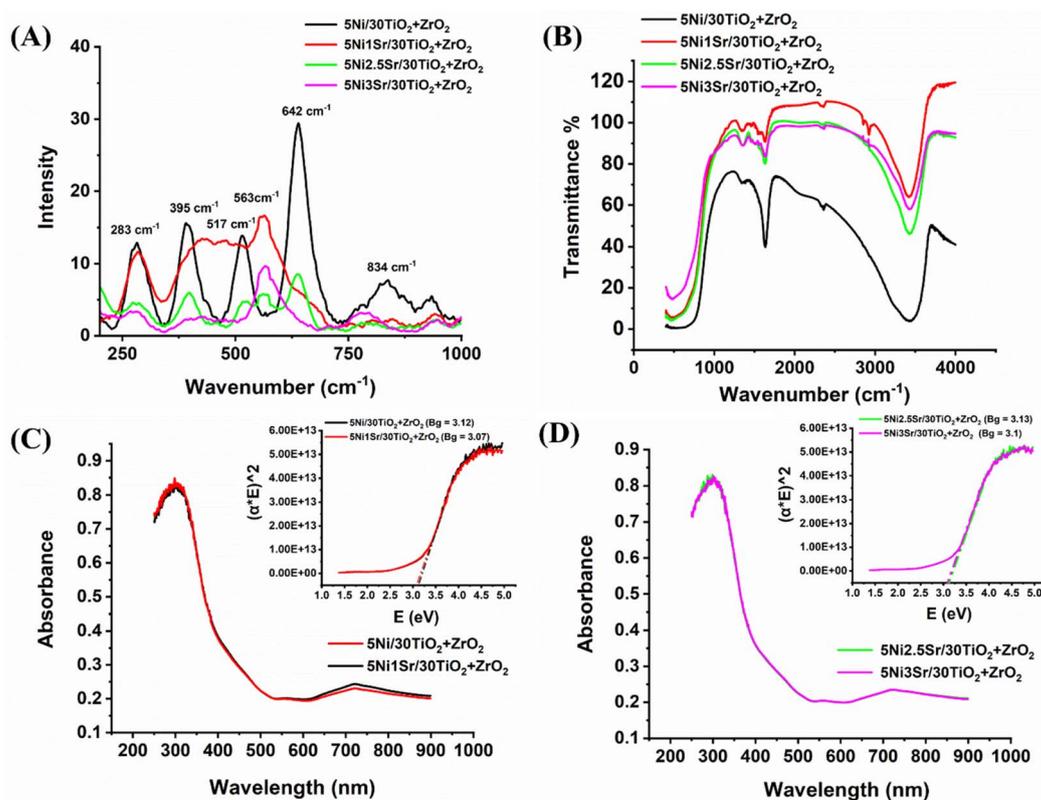


Fig. 4 (A) Raman spectra, (B) infrared spectra (full range), (C) ultra-violet spectra of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni1Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalysts, (D) ultra-violet spectra of 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni3Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalysts.

band for anatase TiO<sub>2</sub> (at 642 cm<sup>-1</sup>) and the B<sub>2g</sub> vibration band for rutile phase (834 cm<sup>-1</sup>) is suppressed, and the new Raman vibration band about 550 cm<sup>-1</sup> for amorphous ZrO<sub>2</sub> phase is appeared.<sup>27</sup> Upon further loading of Sr up to 3% over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>, the intensity of most of the Raman bands declined sharply. Sr addition over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> diminishes the degree of polarizability greatly. Infrared spectra reveal that upon Sr loading, the intensity of the O–H vibration peak (stretching vibration at 2435 cm<sup>-1</sup> and bending vibration at 1638 cm<sup>-1</sup>) is decreased sharply (Fig. 4B). The depletion of surface hydroxyl's intensity upon Sr loading may be due to the formation of Sr–O–M (M = Ti, Zr, Ni) by condensation of SrOH and MOH (M = Ti, Zr, Ni). Even at simple atmospheric conditions, the unpromoted catalyst (5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>) shows the vibration band bidentate formate at 1355 cm<sup>-1</sup> whereas Sr promoted 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst has a vibration band for both bidentate formate at 1355 cm<sup>-1</sup> and ionic carbonate at 1460 cm<sup>-1</sup> (Fig. 4B).<sup>30,31</sup> Sr incorporation does not alter the material's UV absorption properties or the energy gap between its valence and conduction bands (Fig. 4C and D). The bandgap in all catalysts remains at about 3.1 eV. That means Sr addition doesn't affect the electronic transition pattern over the catalyst surface.

### 3.4 H<sub>2</sub>-temperature and CO<sub>2</sub>-temperature programmed profiles

The H<sub>2</sub>-temperature programmed reduction study of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> (x = 1, 2, 2.5, 3) catalysts are

shown in Fig. 5A. The reduction profile of the catalyst at different temperatures indicates the extent of the interaction of reducible species with support. A peak in the reduction process is observed around 600 °C. This suggests the reduction of nickel oxide (NiO) species that moderately interacted with the ESL.<sup>†</sup><sup>32</sup> The CO<sub>2</sub>-temperature programmed desorption profile of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> (x = 1, 2, 2.5, 3) catalysts is shown in Fig. 5B and Table S1.<sup>†</sup> The CO<sub>2</sub> desorption profile of the 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst system is populated with weak basic sites centered at about 100 °C and moderate strength basic sites presented by a broad peak in the range of 150 to 400 °C. The first peak (about 100 °C) is due to the desorption of CO<sub>2</sub> from surface hydroxyl (constituting weak basic sites), whereas the second peak is due to the desorption of CO<sub>2</sub> from surface oxide ions (constituting moderate strength basic sites).<sup>33–36</sup> Upon addition of 1 wt% Sr over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst, the intensity of moderate strength basic sites increases, and a new desorption peak centered about 475 °C also appears. It can be termed as a strong basic site constituted by bonded carbonate species (by Sr<sup>+2</sup>) over the catalyst surface.<sup>37</sup> Overall, it can be said that CO<sub>2</sub> interaction over the catalyst surface is increased at various basic sites upon the addition of basic Sr oxide. Upon 2 wt% Sr loading over 30TiO<sub>2</sub> + ZrO<sub>2</sub>, the CO<sub>2</sub> desorption peak at 420 °C disappeared, and a diffuse peak at about 730 °C appeared, which can be termed as extreme basic sites. 730 °C is reported for the decomposition temperature of SrCO<sub>3</sub>.<sup>38</sup> Over 5Ni2Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst, it can also be noticeable that when a new peak of about 730 °C is



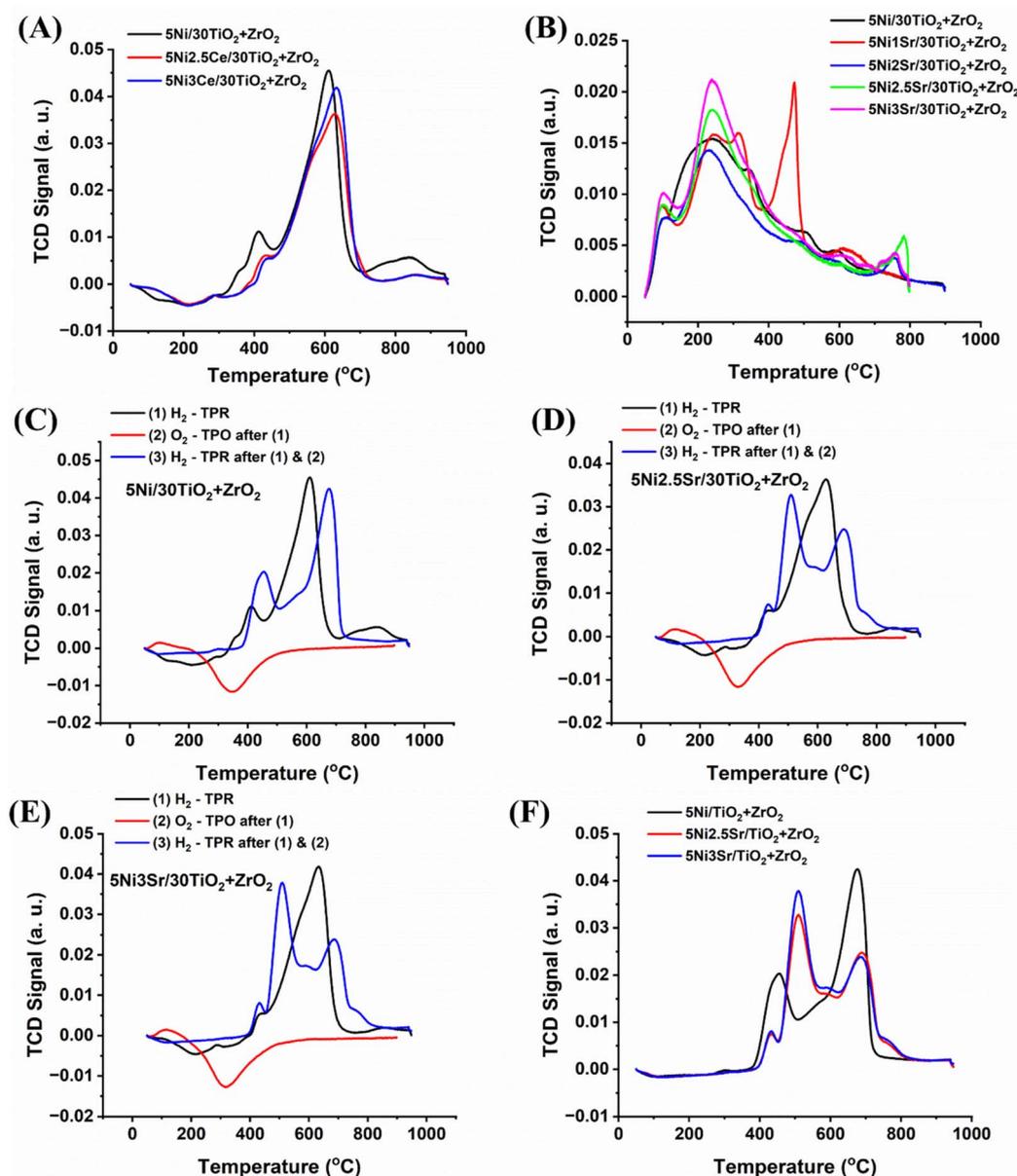


Fig. 5 (A)  $\text{H}_2$ -temperature programmed reduction profile of  $5\text{Ni}/30\text{TiO}_2 + \text{ZrO}_2$  and  $5\text{Ni}_x\text{Sr}/30\text{TiO}_2 + \text{ZrO}_2$  ( $x = 1, 2, 2.5, 3$ ) catalysts, (B)  $\text{CO}_2$ -temperature programmed desorption profile of  $5\text{Ni}/30\text{TiO}_2 + \text{ZrO}_2$  and  $5\text{Ni}_x\text{Sr}/30\text{TiO}_2 + \text{ZrO}_2$  ( $x = 0, 1, 2, 2.5, 3$ ) catalysts, (C) Cyclic  $\text{H}_2\text{TPR}-\text{O}_2\text{TPO}-\text{H}_2\text{TPR}$  profile of  $5\text{Ni}/30\text{TiO}_2 + \text{ZrO}_2$ , (D) cyclic  $\text{H}_2\text{TPR}-\text{O}_2\text{TPO}-\text{H}_2\text{TPR}$  profile of  $5\text{Ni}_{2.5}\text{Sr}/30\text{TiO}_2 + \text{ZrO}_2$ , (E) cyclic  $\text{H}_2\text{TPR}-\text{O}_2\text{TPO}-\text{H}_2\text{TPR}$  profile of  $5\text{Ni}_3\text{Sr}/30\text{TiO}_2 + \text{ZrO}_2$ , (F) the final  $\text{H}_2\text{TPR}$  (from cyclic  $\text{H}_2\text{TPR}-\text{O}_2\text{TPO}-\text{H}_2\text{TPR}$  profile) of  $5\text{Ni}/30\text{TiO}_2 + \text{ZrO}_2$  and  $5\text{Ni}_x\text{Sr}/30\text{TiO}_2 + \text{ZrO}_2$  ( $x = 2.5, 3$ ) catalysts.

surged, the intensity of weak basic sites and moderate strength basic sites are not grown. This can be attributed to the engagement of SrO with  $\text{CO}_2$  and forms  $\text{SrCO}_3$ , constituting an extreme basic site over the catalyst surface<sup>33</sup> Further loading of Sr (2.5 wt%), weak basic sites, moderate strength basic sites, and extreme basic sites are grown. With increasing the Sr loading further to 3 wt%, both weak basic sites and moderate strength basic sites are grown, but the intensity of extreme basic sites declined. Overall, the basic site concentration is grown upon Sr loading over and  $5\text{Ni}/30\text{TiO}_2 + \text{ZrO}_2$  catalyst and  $5\text{Ni}_3\text{Sr}/30\text{TiO}_2 + \text{ZrO}_2$  have the highest amount of basic sites (Table S1†).

POM is carried out over a reduced catalyst system where metallic Ni is the active site. However, it should be noticed that in POM,  $\text{O}_2$  is the oxidizing gas that can oxidize metallic Ni into NiO which turns the active sites inactive. In POM,  $\text{H}_2$  gas is coming out as a reaction product. It is reducing gas also and it can further reduce NiO into Ni. The presence of  $\text{O}_2$  and  $\text{H}_2$  may bring an oxidation–reduction cycle during the POM reaction which may change the reduction profile of the catalyst. To understand the reduction profile and rearrangement of the reduction profile under oxidizing gas ( $\text{O}_2$ ) and reducing gas ( $\text{H}_2$ ) during POM, an  $\text{H}_2\text{TPR}-\text{O}_2\text{TPO}-\text{H}_2\text{TPR}$  cyclic experiment is carried out.



After sequential reduction–oxidation–reduction treatment (by H<sub>2</sub>TPR–O<sub>2</sub>TPO–H<sub>2</sub>TPR cyclic experiment) of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst, the reduction peak is shifted to the higher temperature (from 640 °C). More interestingly, a new reduction peak of relatively less intensity appeared at about 400 °C which is attributed to NiO species having weak interaction with the support (Fig. 5C). That means a major part of NiO species undergoes stronger metal–support interaction and some parts of NiO interact with weak interaction. The high-temperature peak (640 °C) is reduced hardly whereas the low-temperature reduction peak (400 °C) is easily reducible. Interestingly if 2.5–3 wt% Sr promoted 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalysts are sequentially tested for reduction–oxidation–reduction

treatment (by H<sub>2</sub>TPR–O<sub>2</sub>TPO–H<sub>2</sub>TPR cyclic experiment), the low-temperature reduction peak is magnified than the high-temperature peak (Fig. 5D–F). It indicates that over 5Ni2.5Sr/10TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni3Sr/10TiO<sub>2</sub> + ZrO<sub>2</sub> catalysts, the amount of easily reducible NiO is more than hardly reducible NiO species. So, 5Ni2.5Sr/10TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni3Sr/10TiO<sub>2</sub> + ZrO<sub>2</sub> catalysts have more active sites which is derived from easily reducible NiO and available from early temperature ranges.

### 3.5 Catalytic activity results

Generally, zirconia has prominent monoclinic phases, which are unstable, and in the same way, titania has both anatase and rutile phases. Interestingly, 30 wt% titania–70 wt% zirconia has only

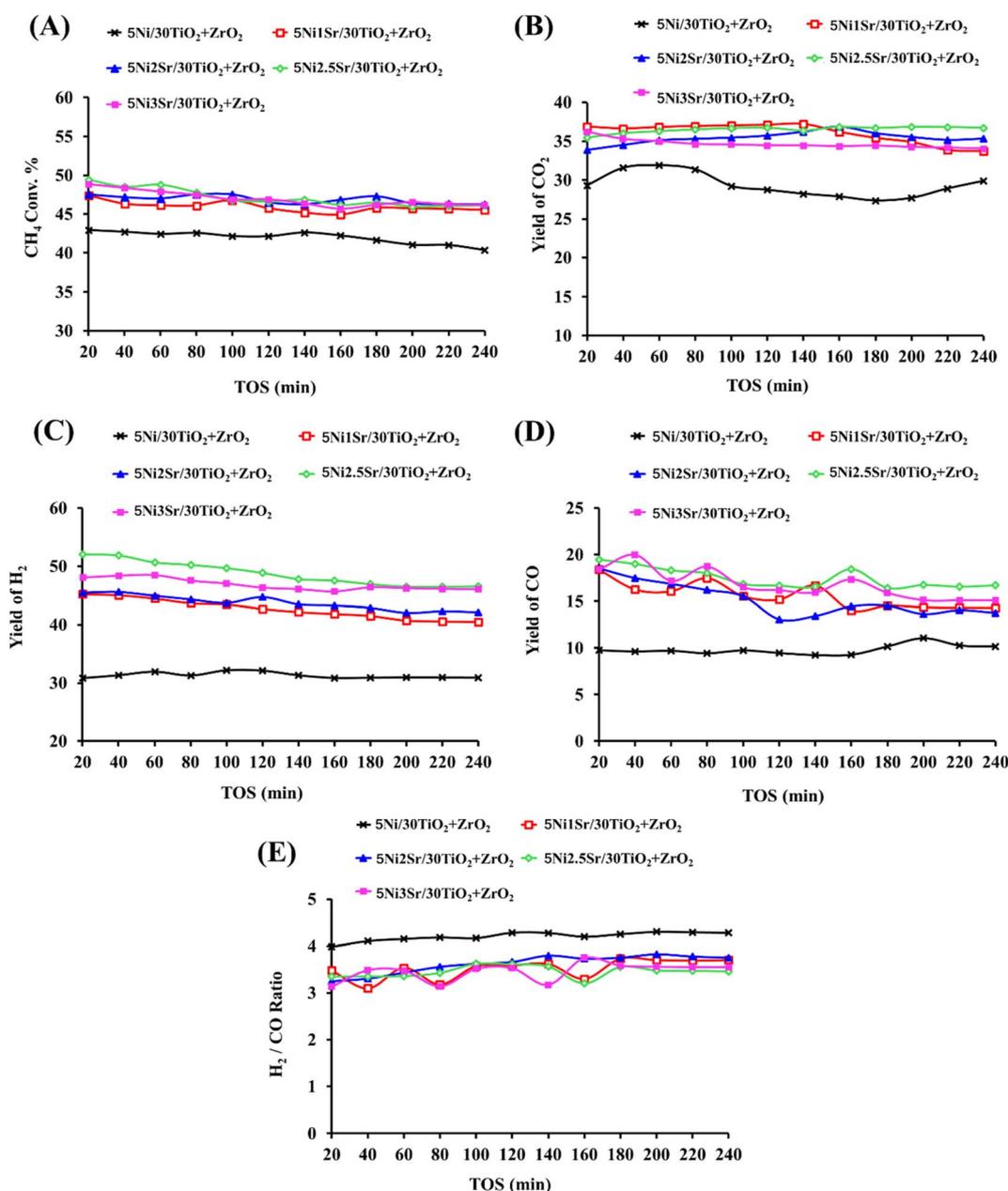


Fig. 6 Time on stream of the catalytic activity results of 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> ( $x = 1, 2, 2.5, 3$ ) catalysts (A) CH<sub>4</sub> conversion (%), (B) CO<sub>2</sub>-yield (%), (C) H<sub>2</sub>-yield (%), (D) CO yield (%), (E) H<sub>2</sub>/CO ratio.



a stable tetragonal zirconia phase and anatase titania phases. That means the presence of titania stabilizes the tetragonal phase of zirconia, whereas the incorporation of zirconia into the titania crystal stabilizes the anatase phase of titania.<sup>27,29</sup> The stable phases of titania–zirconia make it a good choice for supporting the active site “Ni” for partial methane oxidation.

The catalytic activity in terms of CH<sub>4</sub> conversion, H<sub>2</sub> yield, CO yield and H<sub>2</sub>/CO ratio, and CO<sub>2</sub> yield over Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> and Ni<sub>x</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> (*x* = 0, 1, 2, 2.5, 3) catalysts are shown in Fig. 6. NiO is stabilized over a 30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst with moderate strength (as verified by H<sub>2</sub>-TPR). The 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst is reduced before POM in the target of preparing active sites “Ni” for POM reaction. Under the oxidizing gas stream O<sub>2</sub> (which is one of the feeds of POM) and reducing gas stream H<sub>2</sub> (which is one of the products of POM), active sites are reorganized and major of the active sites (Ni) is generated by the reduction of hardly reducible NiO. 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst achieves 43–40% CH<sub>4</sub> conversion during 240 minutes time on stream. In the mean of product distribution, ~30% H<sub>2</sub> yield (H<sub>2</sub>/CO ~4) and ~30% CO<sub>2</sub> yield was maintained for up to 240 minutes on stream. From here, two points should be discussed in more depth. The first one is “equal H<sub>2</sub> yield and CO<sub>2</sub> yield” over a 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst. It indicates the presence of both partial oxidation and total oxidation of methane over titania–zirconia supported Ni catalyst. Jin *et al.* observed that CH<sub>4</sub> was catalysed over metallic Ni surface and gave only gaseous H<sub>2</sub>, whereas NiO catalyses CH<sub>4</sub> and gives CO, CO<sub>2</sub>, and H<sub>2</sub>O.<sup>4</sup> That means NiO is an active site for total oxidation of methane and oxidation of metallic Ni into NiO (by O<sub>2</sub>) can be easily predicted during POM.<sup>39–41</sup> Overall, the *in situ* concentration of both Ni and its oxide (NiO) decides the participation of CH<sub>4</sub> in partial oxidation, in total oxidation, or both. The second point is that the mole of H<sub>2</sub> is about 4 times the mole of CO over an unpromoted catalyst. If H<sub>2</sub> and CO come from a POM reaction over a 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst, the stoichiometric ratio of H<sub>2</sub>/CO may not be more than 2. This indicates that H<sub>2</sub> is also generated by other reaction pathways. This means, the total oxidation reaction takes place and the CO<sub>2</sub> and H<sub>2</sub>O produced will react with methane in dry reforming and steam reforming, respectively.<sup>42</sup> These pathways are known as indirect pathways of POM.<sup>43</sup> Overall, the H<sub>2</sub>/CO ratio ~4 indicates the increased participation of indirect pathways of POM compared to direct pathways. The water gas shift reaction (CO + H<sub>2</sub>O → CO<sub>2</sub> + H<sub>2</sub>) is also feasible in this temperature range (600 °C) and it may also increase H<sub>2</sub>/CO ratio.<sup>2,44,45</sup>

Further, in search of optimum product yield, promotional addition of 1–3 wt% Sr is carried out over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst where Sr is stabilized over catalyst surface by Sr–O–M (M = Ti, Zr, Ni) bond. Adding Sr over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst brings narrower pore size distribution and enhances the formation of stronger basic sites over the catalyst surface. 1 wt% Sr over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst may be specified with the presence of strong basic sites (bonded carbonate species by Sr<sup>+2</sup>), whereas 2–3 wt% Sr promoted 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> has the presence of extreme basic sites (due to SrCO<sub>3</sub>). 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst has the highest population of extreme basic sites among others. During the POM reaction, the active sites are distributed with different interactions with support in the presence of oxidizing gas (O<sub>2</sub>) and reducing gas (H<sub>2</sub>). H<sub>2</sub>TPR-O<sub>2</sub>-TPO-H<sub>2</sub>TPR cyclic profile shows that upon addition of 2.5 wt% Sr over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>, the amount of easily reducible NiO is increased than hardly reducible NiO. So, active sites generated by easily reducible NiO are exposed for POM from a quite early temperature. The CH<sub>4</sub> conversion is enhanced to 47% and 50% over 5Ni1Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> and 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalysts, respectively. However, at the end of 100 minutes, CH<sub>4</sub> conversion over both catalysts reached to 45%. However, at the end of 240 minutes; 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst achieved optimum catalytic activity in mean of higher H<sub>2</sub> yield (47%) and CO<sub>2</sub> yield (37%) than 5Ni1Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst (H<sub>2</sub> yield = 40%, CO<sub>2</sub> yield = 34%). This indicates that extreme basic sites over 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalysts induce POM reactions more towards indirect pathways than 5Ni1Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalysts. The H<sub>2</sub>/CO ratio over 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst is equal to 3.5 which indicates the precise presence of indirect pathways of POM. Upon further loading of Sr (3 wt%) over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>, the active sites distribution profile is similar than 5Ni2Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub>. The concentration of extreme basic sites decreases, whereas the concentration of moderate strength basic sites has grown. Overall, the catalytic activity over 5Ni3Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> is found to be relatively inferior to 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub>. 5Ni3Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> showed 46% CH<sub>4</sub> conversion, 34% CO<sub>2</sub> yield, 46% H<sub>2</sub> yield at the end of 240 minutes on stream.

### 3.6 Process optimization

In the current POM experiment, temperature, O<sub>2</sub>/CH<sub>4</sub> ratio, and space velocity are experimental factors that can be adjusted to get the maximum CH<sub>4</sub> conversion, H<sub>2</sub> yield, and H<sub>2</sub>/CO ratio. Now a days, central composite design (CCD) under response

Table 2 The actual and dimensionless variable of the experimental factors

Experimental factors	Actual value (lower limit & upper limit)	Centre point of the experiment ( $\bar{X}_{oi}$ )	Deviation from the centre of the experiment ( $\Delta x_i$ )	Dimensionless variable ( $X_i$ )
Space velocity (ccg <sup>-1</sup> h <sup>-1</sup> )	10 000	16 000	6000	-1
	22 000			+1
Temperature (°C)	600	700	100	-1
	800			+1
O <sub>2</sub> : CH <sub>4</sub>	0.35	0.55	0.2	-1
	0.75			+1





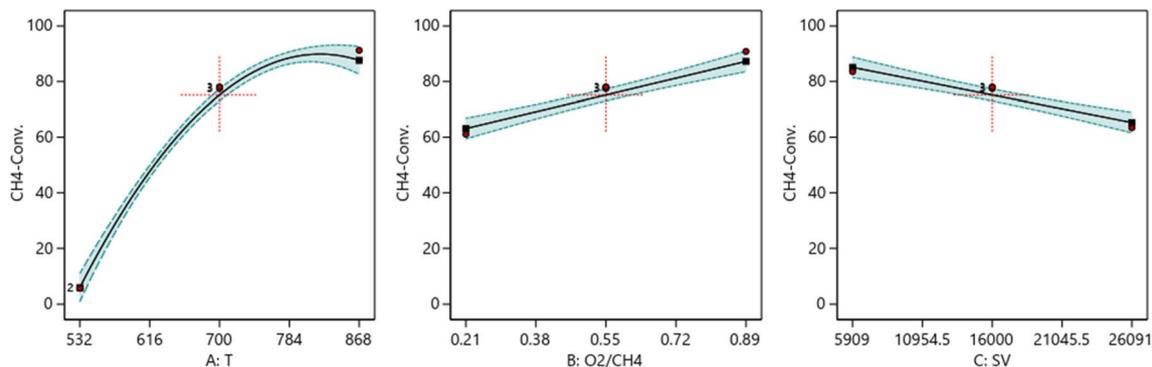


Fig. 7 The relationship between the reaction parameters and CH<sub>4</sub> conversion percentage.

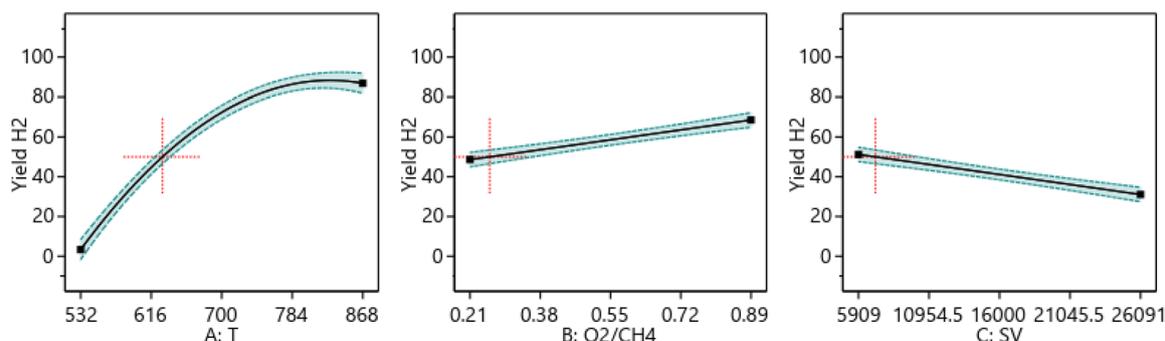


Fig. 8 The relationship between the reaction parameters and yield H<sub>2</sub> percentage.

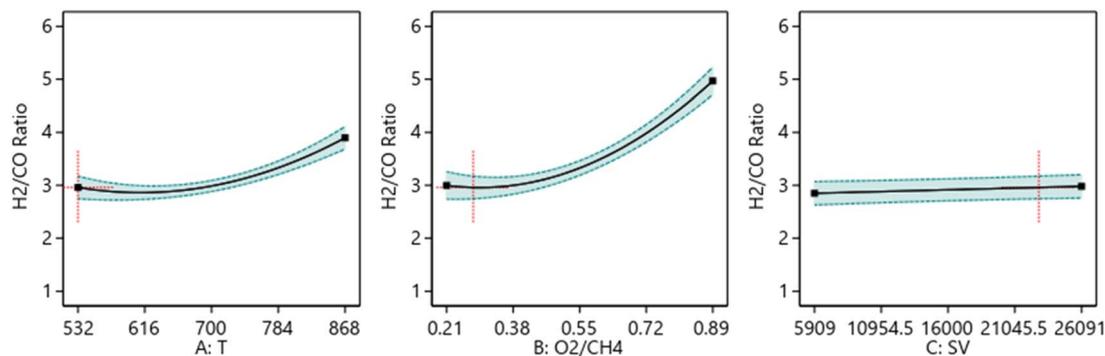


Fig. 9 The relationship between the reaction parameters and H<sub>2</sub>/CO ratio.

ratio, and decreasing the SV value will increase CH<sub>4</sub> conversion. Fig. 8 indicates that increasing temperature, increasing the ratio and decreasing the SV value will increase Yield H<sub>2</sub>. Fig. 9 indicates that increasing temperature, increasing the ratio and increasing the SV value will increase H<sub>2</sub>/CO ratio.

**3.6.1.2 Two factors effect (3D plot).** One factor effect (2D) Plot is not suitable for assessing the relative impact of each factor due to coefficient scaling, and the intercept doesn't align with the center of the design space. Through the aid of the resulting equations, and design expert program the response surface plots were constructed for the predicted conversion or formation of the various components comprising the reaction system

*versus* two process variables while keeping the third at a constant level or value as shown in the 3D models in Fig. 10–15. Fig. 10–11 show the three-dimensional response surface plots, which represents the effects of the factors (Temperature, SV, and ratio O<sub>2</sub>:CH<sub>4</sub>) on the variation of CH<sub>4</sub> conversion. Fig. 10 shows the surface plots which represent the relationship between the response variable (CH<sub>4</sub> conversion), and the two factors (Temperature and the ratio O<sub>2</sub>:CH<sub>4</sub>) at SV = 16 201. It is shown with increasing the temperature and increasing the ratio O<sub>2</sub>:CH<sub>4</sub>, the CH<sub>4</sub> conversion increase. Fig. 11 shows the surface plots that represent the functional relationship between a designated response variable (CH<sub>4</sub> conversion), and the two



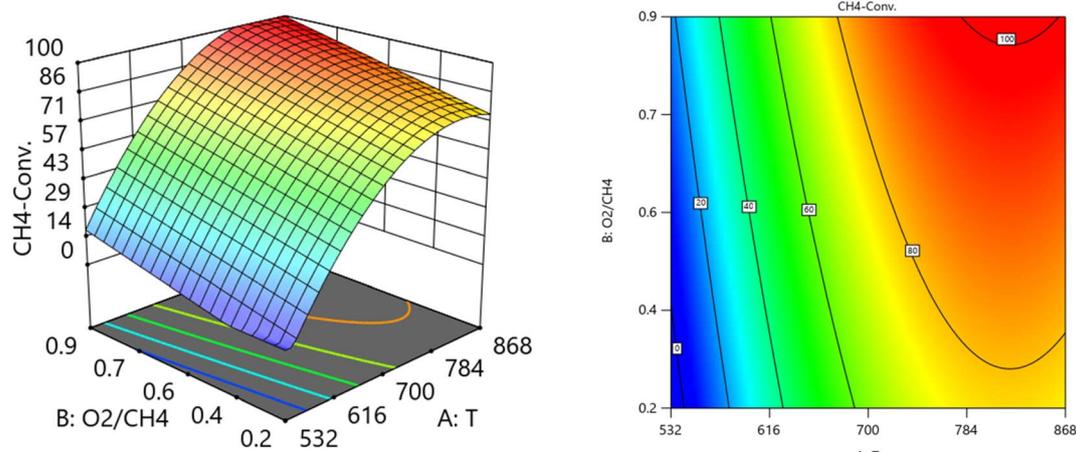


Fig. 10 The relationship between the temperature, ratio, and CH<sub>4</sub> conversion % at SV = 16 201.

factors variables (Temperature and SV) with O<sub>2</sub> : CH<sub>4</sub> fixed at 0.6112. The response surface shows with increasing the temperature and decreasing the SV, the CH<sub>4</sub> conversion increases. It was observed to increase from 5.74% at 600 °C to 97.14% at 800 °C. All factors have significant effects but the temperature has the major effect on the variation of CH<sub>4</sub> conversion.

Fig. 12 and 13 show the three-dimensional response surface plots, which represents the effects of the factors (temperature, SV, and ratio O<sub>2</sub> : CH<sub>4</sub>) on the variation of yield of H<sub>2</sub>. Fig. 12 shows the surface plots which represent the relationship between the response variable (yield H<sub>2</sub>), and the two factors (temperature and the ratio O<sub>2</sub> : CH<sub>4</sub>) at SV = 7119.92. It is shown that by increasing the temperature and increasing the ratio O<sub>2</sub> : CH<sub>4</sub>, the Yield H<sub>2</sub> increases Fig. 13 shows the surface plots that represent the functional relationship between a designated response variable (yield H<sub>2</sub>), and the two factors variables (temperature and SV) with O<sub>2</sub> : CH<sub>4</sub> fixed at 0.4888. The response surface shows with increasing the temperature and

decreasing the SV, the yield H<sub>2</sub> increase. It was observed to increase from 3.18% at 600 °C to 96.32% at 800 °C.

Fig. 14 and 15 show the three-dimensional response surface plots, that represents the effects of the factors (temperature, SV, and ratio O<sub>2</sub> : CH<sub>4</sub>) on the variation of H<sub>2</sub>/CO. Fig. 14 shows the surface plots which represent the relationship between the response variable (H<sub>2</sub>/CO), and the two factors (temperature and ratio O<sub>2</sub> : CH<sub>4</sub>) at SV = 23 000 at. It is shown the lowest H<sub>2</sub>/CO ratio is found at moderate values of both temperature and O<sub>2</sub>/CH<sub>4</sub> ratio, which means neither too high nor too low values of both temperature and SV are optimal for minimizing the H<sub>2</sub>/CO ratio. Fig. 15 shows the surface plots that represent the relationship between the response variable H<sub>2</sub>/CO, and the two factors variables (temperature and SV) with O<sub>2</sub> : CH<sub>4</sub> fixed at 0.3732. The plot shows that the H<sub>2</sub>/CO ratio is firstly influenced by temperature, with higher temperatures leading to lower H<sub>2</sub>/CO ratios, the space velocity has a lesser effect. It was observed to increase from 1.63% at 600 °C to 3.36% at 800 °C.

3.6.1.3 *Model prediction and validation.* Fig. 16 shows optimum predicted simultaneous values of CH<sub>4</sub> conversion,

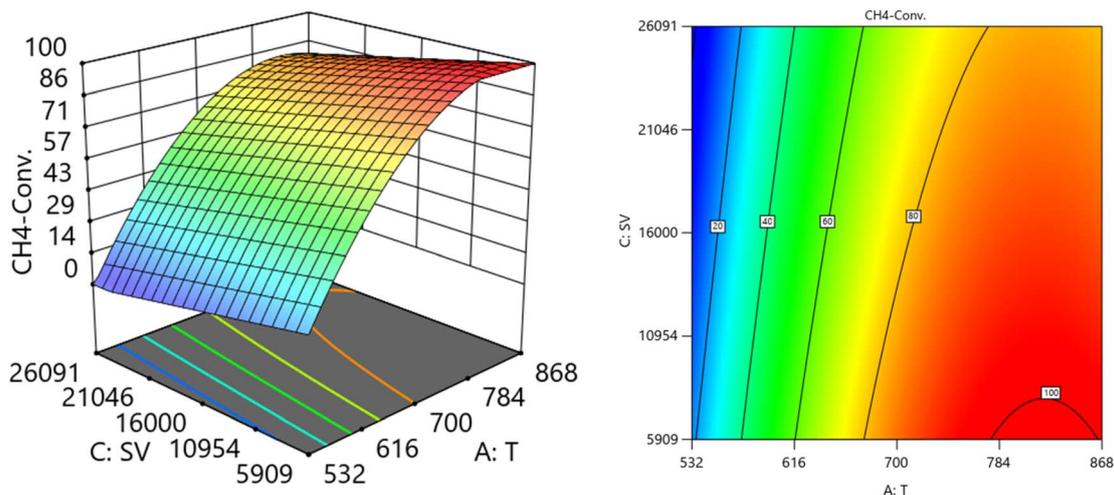


Fig. 11 The relationship between the temperature, SV, and CH<sub>4</sub> conversion % at ratio = 0.6112.



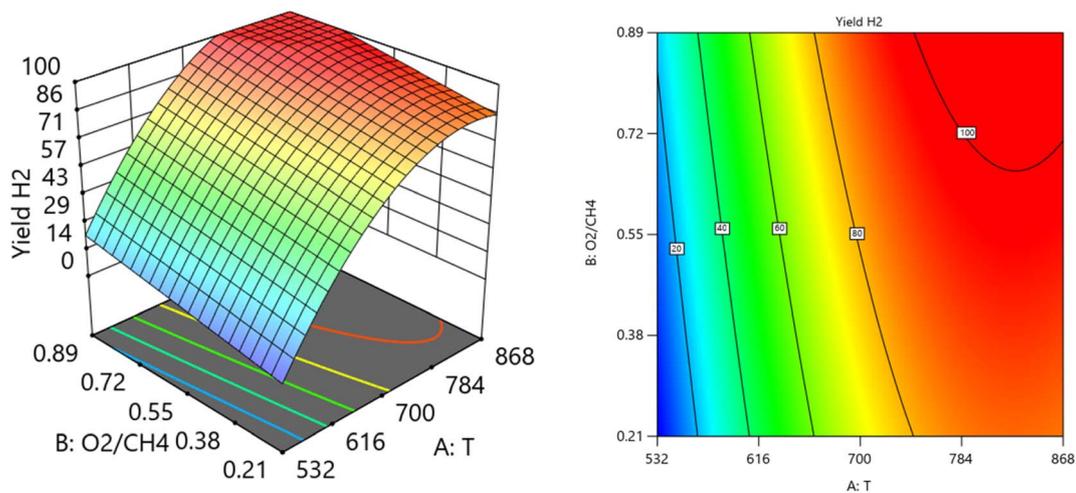


Fig. 12 The relationship between the temperature, ratio, and yield H<sub>2</sub> at SV = 7119.92.

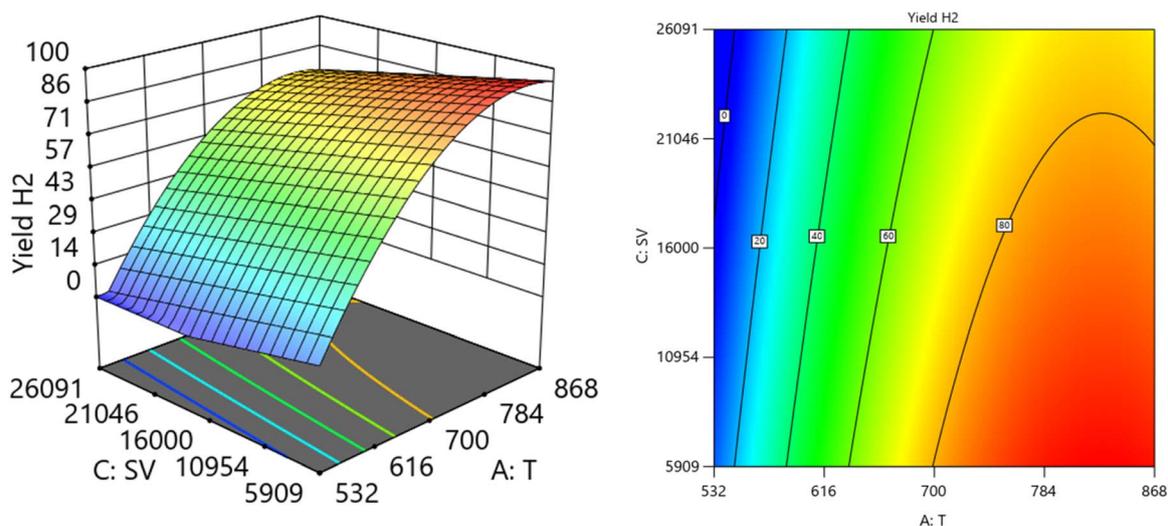


Fig. 13 The relationship between the temperature, SV, and yield H<sub>2</sub> at Ratio = 0.4888.

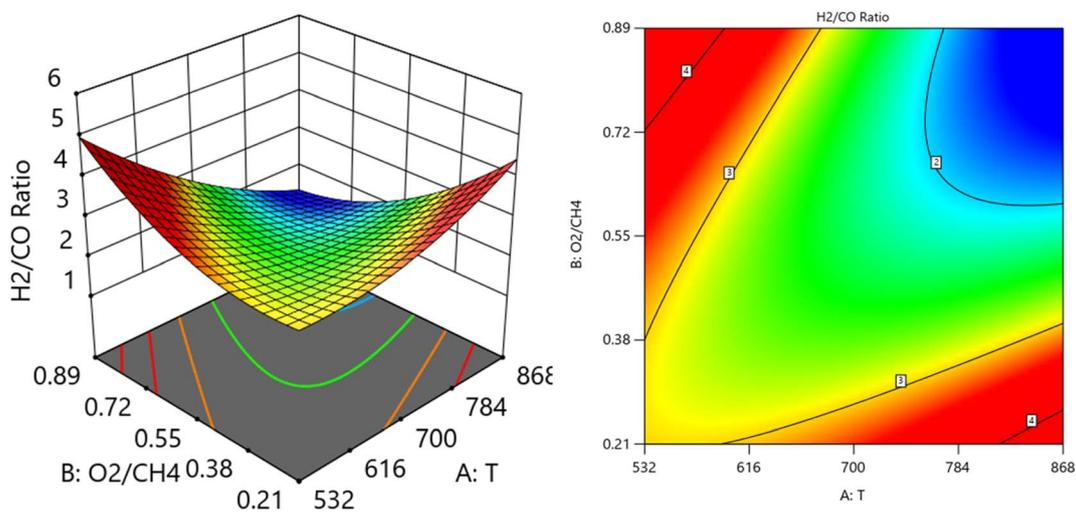


Fig. 14 The relationship between the temperature, ratio, and H<sub>2</sub>/CO at SV = 23 000.



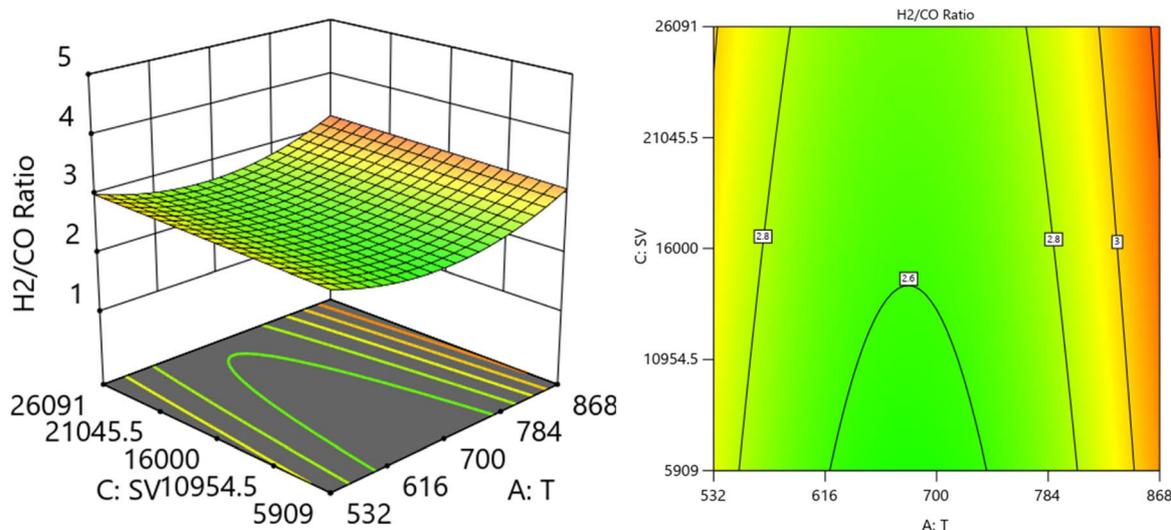


Fig. 15 The relationship between the temperature, SV, and  $H_2/CO$  at ratio = 0.3732.

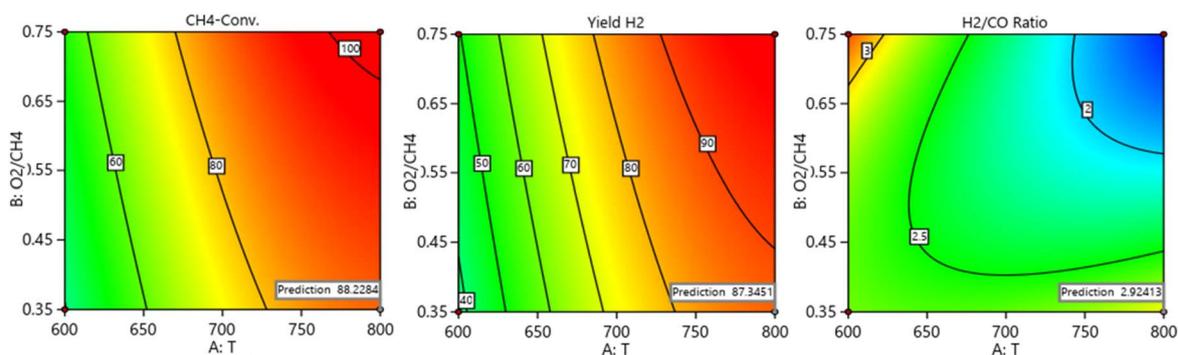


Fig. 16 Optimum predicted simultaneous values of  $CH_4$  conversion, yield  $H_2$ , and  $H_2/CO$  ratio.

Table 4 Comparison of theoretical model predictions and experimental findings

		Variables						
Objective function: max ( $CH_4$ -conv.) & max (yield $H_2$ ) & max ( $H_2/CO$ )		Criteria	T Value	$O_2 : CH_4$ value	SV value	$H_2/Co$ max.	Yield $H_2\%$ max.	$CH_4$ -conv. max.
		Theoretical	800	0.35	10 000	2.924	87.345	88.228
		Experimental	800	0.35	10 000	2.921	86.250	87.850

yield  $H_2$ , and  $H_2/CO$  ratio. Table 4 represents the comparison between predicted with experimental findings. The optimum catalytic activity (88.23%  $CH_4$  conversion, 87.35% yield  $H_2$ , and 2.92 $H_2/CO$ ) towards POM over 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst is predicted at 800 °C reaction temperature, 0.35 $O_2/CH_4$  ratio and 10 000 space velocity (SV). At these given reaction conditions, ~88%  $CH_4$  conversion, 86% yield of  $H_2$ , and 2.92 $H_2/CO$  are achieved experimentally. The closeness of prediction results and experimental results validate the effectiveness of theoretical models.

Further, the best catalyst (5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub>) is investigated for long time on stream (28.5 hours) study at 800 °C, 0.35 $O_2/CH_4$  ratio, and 10 000 space velocity (Fig. S1A and B†) and the spent catalyst is characterized with thermogravimetry

analysis (Fig. S1C†). 44% weight loss is observed over spent 5Ni2.5Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst after 28.5 h time on stream reaction. But, the  $CH_4$  conversion and  $H_2$  yield remains above than 70% during entire time on stream. That means, active sites for POM remains exposed even after high carbon deposit.

## 4. Conclusion

30 wt% titania–70 wt% zirconia (30TiO<sub>2</sub> + ZrO<sub>2</sub>) support has stable tetragonal ZrO<sub>2</sub> and anatase TiO<sub>2</sub> phases, which can stabilize the catalytic active Ni towards POM reaction. During the POM, the active sites undergo re-organization in the presence of oxidizing and reducing gases ( $O_2$  and  $H_2$ ). The majority of these active sites are formed from NiO species that are



scarcely reducible. With equal hydrogen (30%) and CO<sub>2</sub> (30%) yields, the 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst demonstrated 42% CH<sub>4</sub> conversion, suggesting the existence of both partial (producing H<sub>2</sub> and CO) and total (producing CO<sub>2</sub> and H<sub>2</sub>O) oxidation. Due to the presence of a sufficient number of basic sites of moderate strength over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub>, the total oxidation products (CO<sub>2</sub> and H<sub>2</sub>O) interact with the surface, subsequently with CH<sub>4</sub> under indirect pathways and achieve H<sub>2</sub>/CO ~4. The promotional addition of 1 wt% Sr over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst enhances additional strong basic sites, whereas 2.5 wt% Sr addition over 5Ni/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst induces the generation of the highest concentration of extreme basic site. And 5Ni<sub>2.5</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst contains easily reducible NiO too. The easy reducibility promotes methane conversion whereas extreme basicity triggers an indirect pathway of POM by involving total oxidation products, CO<sub>2</sub> and H<sub>2</sub>O, in the oxidation of CH<sub>4</sub>. The high yield of hydrogen (47%) with a ratio of hydrogen to carbon monoxide (H<sub>2</sub>/CO) of 3.5 suggests that these basic sites promote indirect pathways over direct pathways for methane conversion. Further process optimization is carried out over the best catalyst (5Ni<sub>2.5</sub>Sr/30TiO<sub>2</sub> + ZrO<sub>2</sub> catalyst) in the range of 10 00–22000 SV, 0.35–0.75 O<sub>2</sub>/CH<sub>4</sub>, and 600–800 °C reaction temperature by using central composite design under response surface methodology. ~88% CH<sub>4</sub> conversion, 86–87% yield of H<sub>2</sub>, and 2.92H<sub>2</sub>/CO is predicted and experimentally validated at 800 °C reaction temperature, 0.35O<sub>2</sub>/CH<sub>4</sub> ratio, and 10 000 space velocity (SV). Hence, the validation experiment confirmed the correctness of the model since the experimental findings obtained under the expected optimal operating circumstances matched the predicted values pretty well.

## Data availability

All data that support the findings of this study are included within the article.

## Conflicts of interest

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

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