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Insights into promoter-enhanced aqueous phase CO hydrogenation over Co@TiO$_2$ mesoporous nanocomposites

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1. Introduction

The ongoing industrial development has increased the uncontrolled consumption of limited fossil fuel resources. In the future, renewable resources need to be utilized within the energy mix to enable clean and accessible energy for all. Among several alternative energy resources, biomass may play a significant role in the energy sector, where materials such as agro-crops or crop residue can be renewable carbon sources. The most widely used route is gasification, which converts biomass into synthesis gas with carbon monoxide (CO), hydrogen (H$_2$), and methane (CH$_4$) as its major constituents. This biomass-derived syngas (a mixture of CO and H$_2$) is a potential feedstock for the transportation sector’s sulfur-free and heavy metal-free fuels. These fuels are highly demanded to restrict the environment’s negative impact and reduce the dependency on limited fossil fuel resources [1,2].

The Fischer-Tropsch synthesis is typically carried out between 473 and 623 K. These temperatures are high enough to activate and dissociate the reactants molecules (H$_2$ and CO) and, at the same time, low enough to inhibit the associative desorption of surface species (methyl with hydrogen), thus favoring the formation of long-chain hydrocarbons [3]. The selectivity of cobalt-based FTS is strongly dependent on temperature, and the temperature control within the catalyst bed is crucial for its good operability. An isothermal environment can be easily maintained using slurry-bed reactors, which typically use wax as a
reaction medium. However, wax is difficult to separate from the catalyst and product compounds, adding complexity to an industrial operation. Operating the Fischer-Tropsch synthesis in an aqueous phase would easier separate the product compounds from the catalyst. Aqueous phase Fischer-Tropsch synthesis (AFTS) requires lower temperatures to enable the water to remain in liquid form. Operating at low temperatures has thermodynamic benefits for the highly exothermic reaction; however, it kinetically hinders the reaction. It is thus critical to develop a catalyst that has strong performance for aqueous phase Fischer-Tropsch synthesis at low temperatures. So, it very well may be of great interest and worth to utilize a batch reactor to explore the FTS. The batch reactor can make sure that the reactants are distributed evenly so that all the catalysts particles are exposed to the same concentration of gas molecules, and the effect from using long-chain paraffins (wax) in the slurry reactor can be eliminated [4].

The only metals with the required hydrogenation activity for the Fischer-Tropsch synthesis are Co [5-8], Fe [9-11], and Ru [12-14]. Ruthenium nanoparticles have shown promising activity of up to 6.9 mol CO/mol Ru·h at 423 K for aqueous phase FTS [15] and high selectivity towards oxygenates [16]. Ruthenium, however, is not preferred for commercial usage due to its limited availability and relatively high cost [14]. While widely commercially used, iron-based catalysts are not stable in the pure aqueous phase due to their rapid oxidation. The Cobalt-based catalysts are suitable for FTS to synthesize long-chain hydrocarbons due to their high activity, good stability, and low CO2 production [17]. However, it’s challenging to operate cobalt-based FTS in the non-waxy or polar liquid phase, especially in an aqueous medium. One of the attempts was made by Silva et al. for FTS in an ionic liquid [Bmim][NTf2] using Co NPs catalyst, which showed 0.04 mol CO/mol Co·h at 483 K [18]. Another study was carried out by Yan et al. using squalane as a solvent and dispersed Co NPs in it [19]. The catalyst exhibited the catalytic activity of 1.3 mol CO/mol Co·h at 473 K. The breakthrough in the low-temperature FTS over the cobalt-based catalyst was reported by Wang et al. using water as a reaction medium [20]. They reported the water-dispersed PVP stabilized Pt modulated cobalt NPs prepared by a one-step hydrogen reduction process for low-temperature FTS and defined it as an aqueous phase FT synthesis. The 10% Pt-Co catalyst was found to be a very efficient catalyst for aqueous phase FTS. It displayed an activity of 1.1 mol CO/mol Co·h at 433 K. However, the Pt-Co NPs prepared by reduction using NaBH4 displayed lower catalytic activity (0.15 mol CO/mol Co·h) at 433 K compared to hydrogen-reduced Pt-Co NPs. Wang and Kau used LiBET3H and NaBH4 to reduce Co NPs, which displayed quite lower activity of 0.27 mol CO/mol Co·h and 0.09 mol CO/mol Co·h respectively, at 443 K [21]. Most of the catalysts that have been found for AFTS are dispersible nanoparticles. However, supported catalysts have also been observed to be effective for AFTS [22-26]. Moreover, they are easily scalable as well as easy to separate from the reaction systems. Pendyala et al. [24] studied the effect of reaction temperatures on AFTS over a platinum-promoted Co/Al2O3 catalyst. They found that the selectivity of CO2 and CH4 increases slightly with increasing reaction temperature from 418 K to 473 K. Water may further impact the activity of Co-based catalysts positively. For example, computational studies have shown that co-adsorption of CO and water on the active surface may increase the reactivity of CO by reducing the energy barrier for CO dissociation [27]. H2O may impact the mechanism via which hydrocarbons are formed from CO/hydrogenation by behaving as a ‘solvent’ to stabilize the transition state through a hydrogen bond, and as an H-shuttling agent [28]. Another effect of water on FTS was explained by Bertole et al. [29], where the selectivity of methane decreases in the presence of water due to increased surface concentration of active carbon precursor, which leads to higher chain hydrocarbons. Additionally, it is hypothesized that supports such as TiO2 remove the mass-transport restriction by condensing water in the catalyst pores. Hence, they are thought to give accessibility to the mass-transport limited regions [8,30]. However, the stability of cobalt in the presence of water may be limited for small particles. A thermodynamic guide was formulated stating that cobalt crystallites with less than 4.4 nm could oxidize if the water ratio to hydrogen is less than 1.5 (at 493 K) [31]. Thus, operating at a relatively high temperature would require a high partial pressure of hydrogen to keep the crystallites in a reduced state.

| Table 1 | Consists of comparative data reported for AFTS in the literature. It has been observed that Ru-based catalysts (entry 1–5) are highly active for AFTS processes, which can relate to the high stability of metallic ruthenium in the aqueous medium. However, Ru NPs or supported Ru catalysts are also selective for oxygenates hence compromise the required hydrocarbons selectivity. Also, the high costs of ruthenium and its larger amount make it less preferable than cobalt catalysts. For Pt-Co catalyst (entry 6) contains high loading of Pt (10%), with comparatively low activity and high methane. Supported Pt-Co catalyst (entry 7) has also been reported to give high catalytic activity (including CO2) nevertheless at high temperature (473 K), with C2H6 selectivity of 70% and high selectivity for CO2 and CH4.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Hydrocarbon yield</th>
<th>Temperature (K)</th>
<th>Water H2 ratio</th>
<th>CO2 selectivity</th>
<th>CH4 selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co [5-8]</td>
<td>60%–80%</td>
<td>418 K</td>
<td>1.5</td>
<td>20%</td>
<td>80%</td>
</tr>
<tr>
<td>Fe [9-11]</td>
<td>50%–70%</td>
<td>438 K</td>
<td>2</td>
<td>30%</td>
<td>70%</td>
</tr>
<tr>
<td>Ru [12-14]</td>
<td>50%–60%</td>
<td>473 K</td>
<td>1.5</td>
<td>40%</td>
<td>60%</td>
</tr>
<tr>
<td>Co [15]</td>
<td>65%–75%</td>
<td>453 K</td>
<td>1</td>
<td>30%</td>
<td>70%</td>
</tr>
<tr>
<td>Co [18]</td>
<td>50%–60%</td>
<td>483 K</td>
<td>2</td>
<td>25%</td>
<td>75%</td>
</tr>
</tbody>
</table>

2. Experimental section

2.1. Materials and methods

All the chemicals, solvents, and metal precursors used in this work are obtained from Sigma Aldrich and used without further purification or modification. All the required gases were purchased from Sigma Gas service, having purity higher than 99.99%.

2.2. Preparation of the catalyst

In the typical synthesis process (Scheme 1), 5.6 g of titanium iso-propanol was dissolved in 50 mL of ethanol with 2 mL of HNO3 and kept under vigorous stirring for 6–7 h at room temperature. The required amount of Co(NO3)2·6H2O was added to 35 mL of ethanol containing P123 (Pluronic triblock copolymer, EO20–PO70–EO20) as the structure-directing agent and placed under stirring for 2 h. The two solutions were mixed and are stirred overnight. The final solution was evaporated up to dryness at 333 K for 12 h and calcined at 673 K for 5 h. The amount of Co(NO3)2·6H2O was altered to obtain different cobalt loadings. Similarly, along with Co(NO3)2·6H2O, a calculated amount Mn(NO3)2·6H2O and H2PtCl6·H2O was added to the solution, allowed to rotate for some time, and followed the same conditions for drying and calcination as mentioned for the catalyst without promoters.

Catalyst with different loadings of cobalt 1P15C, 1P20C, 1P25C, 1P30C, manganese 1.5M1P25C, 3M1P25C, 6M1P25C, 12M1P25C, and platinum 3 M0.5P25C, 3 M0.25P25C were prepared by varying the respective amount of metal salts of the different elements to prepare various catalysts (see Table S1). The catalysts with different cobalt, platinum, and manganese proportions are represented as xMyPzC, where x, y, and z represent the different wt.% of manganese platinum, and cobalt respectively, on mesoporous titanium dioxide.

2.3. Analytical measurements

The N2 adsorption–desorption isotherms were recorded on a J. Gahtori et al.
Micromeritics ASAP 2020 to investigate the pore architecture in the prepared catalyst. The catalyst was degassed in a vacuum at 623 K before every measurement.

Proto Advance X-ray diffractometer with Cu Kα radiation connected with a Lynx eye high-speed strip detector was used to record the X-ray diffraction pattern. For the phase identification of reduced catalysts by XRD, all the samples were reduced at 673 K with 20% H2 in N2 and cooled to room temperature. The flow of N2O passivated the reduced samples for 30 min before the XRD measurement. XRD was measured at ambient temperature by 30 kV X-rays in the range of 2θ = 10–80° with a step size.

The Thermo Scientific K-alpha X-ray photoelectron spectroscopy (XPS) was used to measure the oxidation state of various active metals present in the samples. The binding energy of C 1 s at 284.8 eV was used as a reference to calibrate the binding energies of every element.

Transmission electron microscopy (TEM) images were recorded by JEM 2100 (JEOL, Japan). A minimal amount of catalyst was suspended in ethanol, and it was sonicated for 10–15 min. 2–3 drops were cast on a Cu grid supported with lacey carbon, and it was allowed to dry for some time to capture the images.

Temperature programmed reduction (TPR), hydrogen chemisorption and pulse reoxidation, and CO-temperature programmed desorption (TPD) were carried out using Micromeritics Auto Chem II 2920 instrument. To obtain TPR signals, the catalyst was flushed initially with helium at 623 K for 2 h, and it was cooled down to room temperature. Subsequently, a flow of 20% H2 in He was passed over the catalyst while raising the temperature linearly to 1173 K (heating rate: 10 K/min). The change in the H2 concentration in the effluent was observed by the thermal conductivity detector (TCD). The H2 chemisorption and pulse reoxidation experiments were carried by following a previously reported procedure [32,33]. After TPD of H2, the sample was reoxidized by pulses of pure O2 in helium carrier at activation temperature, then calculated the number of moles of O2 consumed. The percentage reduction was calculated assuming that Co3+ re-oxidized to Co4O6.

The total amount of cobalt in the catalyst before and after the reaction was analyzed by AAS, using Solaar M6 Dual Zeeman. The amount of Pt and Mn were confirmed by ICP-AES using the M/s Leeman Labs instrument.

2.4. Investigation of catalytic performance for CO hydrogenation

The catalysts for AFTS were tested in a high-pressure stainless steel 100 mL batch reactor (Parr instrument). Before the reaction, about 0.5 g of the freshly prepared catalyst was reduced at 673 K with 20% H2 in N2 for 16 h. After cooling, the reduced catalyst was passivated with the flow of N2O, and the catalyst was dispersed in 40 mL of water and transferred to the reactor. It was purged two times with the reaction mixture gas (CO: H2: N2 = 1: 2: 1/3) to avoid impurities, and then it was sealed and pressurized till 3.0 MPa by reaction gas mixture (unless mentioned). CO hydrogenation proficiency was measured at the range 433–473 K at 700 rpm stirring speed. For every catalyst, the reaction was carried out for 20 h once it reached the reaction temperature.

After completing the reaction, the reactor was cooled to RT, and the gaseous products were analyzed with an online gas analyzer (Agilent 7890B) coupled with the reactor. The gases H2, CO2, N2, CH4, CO, and C2–C3 were separated on a Molsieve 5A column and analyzed with a
thermal conductivity detector (TCD). The gaseous C4 hydrocarbons were separated on an HP-PONA column and analyzed with a flame ionization detector (FID). The liquid hydrocarbons were extracted by cyclohexane addition to the reaction mixture in the autoclave. The organic layer containing cyclohexane was decanted, and the organic compounds (mainly alkanes and alkenes) were analyzed using an HP-PONA column attached with FID. The composition of the aqueous phase was analyzed by gas chromatographically using a DB-WAX column attached with FID.

The CO conversion rate of the catalyst and selectivity of each reaction has been defined by the following equations [24]:

\[
\text{CO conversion rate} = \frac{\text{rate of CO consumption}}{(\text{moles of CO converted} \times \text{reaction time})}
\]

\[
\text{Selectivity} = \frac{\text{moles of C formed as products}}{\text{moles of cobalt used} \times \text{reaction time}}
\]

2.5. Kinetic analysis

A kinetic analysis was performed for optimized catalyst 3M1P25C using an aqueous phase batch reactor at 300 K, 30.4 bar (starting pressure) with 40 mL of water in slurry. The catalyst was reduced and tested (in the 100 mL batch reactor) using the same method for catalyst performance. Five runs were performed, with different reaction times (1 h, 5 h, 10 h, 15 h, and 20 h), after which the CO conversion, end-time reactor pressure, and selectivities of CO and CO₂ were determined from the gradient of the curve N and thermal conductivity detector (TCD). The gaseous C4 hydrocarbons were extracted by cyclohexane addition to the reaction mixture in the autoclave. The organic layer containing cyclohexane was decanted, and the organic compounds (mainly alkanes and alkenes) were analyzed using an HP-PONA column attached with FID. The composition of the aqueous phase was analyzed by gas chromatographically using a DB-WAX column attached with FID.

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\]

\[
\text{Selectivity} = \frac{\text{moles of C formed as products}}{\text{moles of cobalt used} \times \text{reaction time}}
\]

2.5. Kinetic analysis

A kinetic analysis was performed for optimized catalyst 3M1P25C using an aqueous phase batch reactor at 300 K, 30.4 bar (starting pressure) with 40 mL of water in slurry. The catalyst was reduced and tested (in the 100 mL batch reactor) using the same method for catalyst performance. Five runs were performed, with different reaction times (1 h, 5 h, 10 h, 15 h, and 20 h), after which the CO conversion, end-time reactor pressure, and selectivities of CO₂, CH₄, and hydrocarbons were recorded. The rate of the Fischer-Tropsch synthesis is a function of the partial pressure of reactants, CO conversion, and time. While rates of CO consumption recorded in the catalytic performance analysis are based on the average rate over the total reaction time (12 h), the kinetic analysis was performed using instantaneous rates at specific time intervals. These experimental rates of reaction are determined by the differential change in the number of moles of CO within the reaction system according to the following expression.

\[
dN_{CO} = -r_{FT} \, w
\]

Where \( N_{CO} \) is the number of moles of CO within the reaction system after its time in hours, \( -r_{FT} \) is the CO conversion rate as a function of moles of cobalt in an aqueous phase batch reactor, and \( w \) is the rate of cobalt. The change in the number of moles of CO with time (see Fig. S1) was determined from the gradient of the curve \( N_{CO} \) vs. time and analyzed both analytically (using an empirical fitted curve) and numerically with an insignificant difference in this range.

The data was fitted by least squares regression to various macro kinetic rate expressions [34–37]. The rate expression was populated with partial pressures of CO and H₂ at each time interval, considering the partial pressure changes due to conversion and overall pressure changes within the reaction system as a function of time. For rate expressions, including the partial pressure of water in the system [34,36], only reaction water was considered.

3. Results and discussion

3.1. Characterization

3.1.1. \( N_2 \) physisorption study

The textural properties for all the catalysts are shown in Table 2, while the \( N_2 \) adsorption–desorption curves are depicted in Fig. 1. The nitrogen sorption isotherms display type IV isotherm with an H1 hysteresis loop, typical of mesoporous materials with cylindrical pores [38]. The change in the hysteresis loop of TiO₂ upon metal addition indicates the notable change in the textural property of the surface. Their relative pressure of 0.70–0.75 shows a sharp uptake of \( N_2 \) due to \( N_2 \) condensation in the pores formed by particles on the surface. BJH pore size distribution for TiO₂ and Co-Pt deposited TiO₂ in Fig. 1b indicates the distribution range of 4–8 nm, while it is between 4 and 10 nm in Mn, Co, and Pt deposited TiO₂ (see Fig. 1d). TiO₂ shows a high surface area of 176 m²/g with an average pore size of 7.6 nm and a total pore volume of 0.14 cm³/g. However, increasing the amount of deposited metal increases the surface area, pore diameter, and pore volume in the range of 198–299 m²/g, 7.8–7.9 nm, and 0.17–0.30 cm³/g, respectively, which indicates a strong impact of metals on the structural properties of the support.

The obtained increase in the surface area upon deposition of cobalt on mesoporous titania was also reported by Deshmukh et al. [72]. The change in the textural property of TiO₂ can be associated with the difference in the crystallization behavior of TiO₂ after metal loading. The crystallite size of TiO₂ increases due to calcination, which leads to the relaxation of mesoporous structure [39]. However, the addition of external metal on TiO₂ could prevent its crystallite size extension and improve its surface properties. So, the surface area is inversely proportional to the degree of crystallization. So, the increased surface area after metal deposition implies that mixing two materials with different particle sizes could change the surface areas, pore diameter, and pore volume without changing the support. The surface area of active metal can be greater than support itself, and depositing it on such support can positively modify its surface properties.

3.1.2. X-ray diffraction

The powder XRD pattern for TiO₂, unreduced and reduced 1PzC, xM1P25C, and 3MyP25C samples are depicted in Fig. 2. The diffraction lines of pure anatase are dominating in all freshly prepared and reduced catalysts and exhibit the characteristic peaks at 2θ = 24.9°, 37.8°, 48.0°, 53.9°, 54.6°, 69.49°, 70.3°, and 75.3° (JCPDS-00-021-1272) indexed as the (101), (004), (200), (105), (211), (204), (220), and (215) planes respectively. No significant diffraction peaks for the Co₃O₄ phase are visible in the diffractograms (see Fig. 2a & 2b) of unreduced catalysts, which implies that even with the high loading of cobalt, Co₃O₄ particles

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Composition (at. %)</th>
<th>Surface area (m²/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>–</td>
<td>176</td>
<td>7.6</td>
<td>0.12</td>
</tr>
<tr>
<td>1P15C</td>
<td>0.14</td>
<td>198</td>
<td>7.6</td>
<td>0.14</td>
</tr>
<tr>
<td>1P25C</td>
<td>0.14</td>
<td>221</td>
<td>8.1</td>
<td>0.15</td>
</tr>
<tr>
<td>1P25C</td>
<td>0.12</td>
<td>215</td>
<td>8.5</td>
<td>0.16</td>
</tr>
<tr>
<td>1P50C</td>
<td>0.12</td>
<td>243</td>
<td>8.0</td>
<td>0.18</td>
</tr>
<tr>
<td>1.5M1P25C</td>
<td>0.12</td>
<td>202</td>
<td>8.2</td>
<td>0.20</td>
</tr>
<tr>
<td>3M1P25C</td>
<td>0.13</td>
<td>229</td>
<td>7.9</td>
<td>0.22</td>
</tr>
<tr>
<td>6M1P25C</td>
<td>0.15</td>
<td>223</td>
<td>8.2</td>
<td>0.18</td>
</tr>
<tr>
<td>12M1P25C</td>
<td>0.22</td>
<td>212</td>
<td>7.6</td>
<td>0.26</td>
</tr>
<tr>
<td>3 M0.25P25C</td>
<td>–</td>
<td>223</td>
<td>8.0</td>
<td>0.21</td>
</tr>
<tr>
<td>3 M0.5P25C</td>
<td>–</td>
<td>222</td>
<td>7.3</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Note: xMyPzC represents a catalyst where x, y, and z denote the different wt.% of manganese, platinum, and cobalt, respectively, on mesoporous titanium dioxide
are highly dispersed as small particles over the TiO\textsubscript{2} surface, or they are beyond the limit of X-ray diffraction. Also, no distinct diffraction lines are visible, which can attribute to the mixed cobalt-titanate oxide (the most intense line appears at 2\(\theta\) = 32.8°) spinels. The different reduced samples of Co supported on TiO\textsubscript{2} (see Fig. 2 c) exhibit the characteristic reflections for hcp-Co at 2\(\theta\) = 41.2°, 44.0°, and 47.0° indexed as reflections to the (1 1 1), (2 0 0) and (2 0 0) planes respectively (the last reflection may be overlapped with the broad reflection of (2 0 0) plane of anatase). No distinctive peaks are observed for Pt due to the low amount of platinum in the sample or its high dispersion on TiO\textsubscript{2}. In the reduced samples, some diffraction lines of TiO\textsubscript{2} shift towards lower diffraction angles, which indicates that there may be lattice relaxation in the interstitial positions of the lattice of TiO\textsubscript{2}(Ti\textsuperscript{4+} = 0.68 Å) due to the presence of cobalt ions (Co\textsuperscript{2+} = 0.74 Å) [40].

Fig. 2d shows the XRD patterns for the different manganese-loaded 1P25C catalysts (reduced) along with two different amounts of platinum-loaded 3M25C catalyst after reduction. The catalyst with high manganese content (Mn/Co = 0.5) shows evidence of MnTiO\textsubscript{3} with reflections at 2\(\theta\) = 31.9°, 35.3°, 40.1°, 52.8°, and 61.2° indexed as (1 0 4), (1 1 0), (1 1 3), (1 1 6), and (1 2 4) phases (JCPDS-00–029–0902), alongside those of anatase and hcp-Co. Manganese titanate, MnTiO\textsubscript{3}, could have been formed during reduction/calcination, where Mn\textsuperscript{2+} (Mn\textsuperscript{2+} = 0.82 Å) ions might have been entered into the interstitial position or directly at Ti\textsuperscript{4+} sites in TiO\textsubscript{2} lattice. The absence of any visible reflections in the XRD pattern for any oxide form of manganese in the catalyst loaded with the low amount of manganese (Mn/Co less than 0.5) presumed its high dispersion, which can create a more significant fraction of cobalt being in contact with manganese [41]. The different amounts of platinum on the 3M25C catalyst do not significantly affect the diffraction lines of TiO\textsubscript{2} and hcp-Co phases present in the reduced catalysts.

3.1.3. X-ray photoelectron spectroscopy

The XPS spectra of Ti 2p for 1PzC samples, Co 2p for 1PzC and xM1P25C samples, and Mn 2p for xM1P25C samples are depicted in Fig. 3. For Ti 2p (see Fig. 3a) in 1P30C catalyst, the peak centered at 458.8 eV and 464.4 eV are assigned to Ti\textsuperscript{4+} 2p\textsubscript{3/2}, and Ti\textsuperscript{4+} 2p\textsubscript{1/2} respectively. The small intensity peak that appears at 459.6 eV indicates the presence of Ti\textsuperscript{3+} 2p\textsubscript{3/2}. The localization of charge carriers by foreign atoms may create oxygen vacancies, which can be a reason for the
presence of the Ti\(^{3+}\) state [42]. The redshift in the binding energy of Ti\(^{4+}\) 2p\(_{3/2}\) and Ti\(^{4+}\) 2p\(_{1/2}\) in the catalyst with low cobalt loading suggests the intercalation of cobalt and oxygen vacancy creation in the lattice titania, which increases the electron density on Ti\(^{4+}\) [43,44]. The small clusters of metal are reported to interact strongly with the support compared to the large crystals. So, the extent of intercalation of foreign metal ions in the lattice of titania decreases with the high loading of external metal. It is also revealed by the increase in the relative peak intensity of Ti\(^{3+}\) 2p\(_{3/2}\) at higher loading of cobalt (see Table S2).

The deconvoluted peak (see Fig. 3b) at binding energy of 780.8 eV and 796.6 eV indicate the presence of Co\(^{3+}\) 2p\(_{3/2}\) and Co\(^{3+}\) 2p\(_{1/2}\), while the peaks at 782.9 eV and 798.5 eV are assigned to Co\(^{2+}\) 2p\(_{3/2}\) and Co\(^{2+}\) 2p\(_{1/2}\) respectively [45]. The binding energy difference of \(\Delta E = 15.7\) eV between Co\(^{3+}\) 2p\(_{3/2}\) and Co\(^{3+}\) 2p\(_{1/2}\) shows that cobalt is mainly present in the Co\(_3\)O\(_4\) phase in each catalyst after calcination, and the peak intensity increases with increasing the cobalt loading [46]. The strong satellite peak at 787 eV and 803.5 eV was assigned to the Co\(^{2+}\) state, revealing the possible formation of CoO or CoTiO\(_3\) due to calcination [47]. The Co 2p spectra for Mn-Co catalysts display the same number of peaks. However, they shifted slightly towards lower binding energy, possibly caused by Mn-Co interactions.

For Mn 2p, the doublet appeared at 641.6 eV, and 653.4 eV are
assigned to Mn 2p\textsubscript{3/2} and Mn 2p\textsubscript{1/2}. Further, the deconvolution of Mn 2p\textsubscript{3/2} peak gave two peaks at 641.6 eV and 645 eV (see Fig. 3d), which attributed to Mn\textsuperscript{3+} (MnO) and its satellite peak \[48\]. The Pt 4f spectra (see Fig. 3e) is deconvoluted into four peaks at 71.4–70.8, 72.6, 74.3 and 75.8 eV, which correspond to Pt\textsuperscript{0} 4f\textsubscript{7/2}, Pt\textsuperscript{2+} 4f\textsubscript{7/2}, Pt\textsuperscript{0} 4f\textsubscript{5/2}, and Pt\textsuperscript{2+} 4f\textsubscript{5/2} respectively. The relative areas under the Pt\textsuperscript{0} and Pt\textsuperscript{2+} peaks indicate that most of the platinum exists as Pt\textsuperscript{2+} state in the freshly prepared materials. Some Pt\textsuperscript{0} might be formed due to auto reduction during calcination. The blue shift in the binding energies of platinum, with high cobalt loading, indicates the possible alloy formation of platinum with

Fig. 3. XPS spectra for (a) Ti 2p in 1PzC, (b) Co 2p in 1PzC, (c) Co 2p in xM1P25C, (d) Mn 2p in xM1P25C, and Pt 4f in 1PzC.
catalyst support and high specific surface area (>100 m² g⁻¹) of the catalysts, the sizes of Co₃O₄ particles can also be calculated using a simplified K–M formula from XPS data [50]. The calculated results are presented in Table 3.

3.1.4. Temperature programmed reduction analysis:

The reducibility of the samples is investigated using TPR (see Fig. 4). The previous reports had shown that reduction of Co₃O₄ occurs in two steps, with Co₃O₄ reducing to CoO followed by the reduction of CoO to metallic cobalt [52,53]. However, in all our investigated samples, the individual peaks correspond to subsequent reduction steps for Co₃O₄ to CoO are nearly indistinguishable similar to the previously reported by Kveta et al. [53], Arnoldy et al. [54], and Petersen et al. [55]. The TPR peaks for 25 wt% Co loaded on TiO₂ (see Fig. 4a) in the absence of platinum shows the temperature maxima > 673 K for the reduction of Co₃O₄. The addition of 1 wt% Pt shifts the reduction peak to a lower temperature, resulting from the H₂ spillover effect from Pt to Co₃O₄ [56]. The increased relative intensity of the reduction shoulder with high cobalt loading indicates the increase in the average cluster size, resulting in the loss of interaction with support. The small size and highly dispersed particles interact strongly with the support and can be responsible for the broadening of reduction shoulders [33]. The absence of any reduction peak at the high temperature indicates that the formation of bulk cobalt-titanate species is almost negligible or non-reducible up to the reported temperature if formed [57].

Fig. 4b and Fig. 4c depict the TPR profiles for different manganese loaded 1P25C (xM1P25C) samples and different platinum loaded 3M25C (3MyP25C) samples. The two reduction peaks below 473 K can be assigned to H₂ consumption by two different physically adsorbed oxygens at the oxygen vacant sites created either in MnTiOₓ or Co,MnₓOₓ oxide spinels [58,59]. Since these two peaks (less than 473 K) are absent in 1P25C samples, it can be assumed that these low reduction peaks are the consequences of adding Mn to the catalyst. Although it is reported that the addition of manganese hampers the reduction of cobalt, however, the different preparation procedures can cause significant changes in the TPR profiles [41,60].

Interestingly, with the addition of the small amount of manganese to 1P25C, the reduction of CoO occurs at 30 K lower than the unpromoted catalyst (peak II, shifts from 700 to 670 K). Therefore, this observation specifies that adding a small amount of manganese can improve the reducibility of cobalt, which can be directly related to the increase in the catalytic activity of these samples by stabilizing the cobalt particles [61], which we will be seen later. With the higher loading of manganese, the reduction temperature shifts to a higher value, which can be due to the encasement of Co particles by Mn, especially in the higher loading.

The rest of the two plots (see Fig. 4c) are for two different loadings of platinum on 3M25C (3MyP25C) catalysts. A small increment in the reduction temperature is observed by decreasing the amount of platinum to 0.5 wt% and 0.25 wt%. Since the small amount of manganese contributes to the enhancement of cobalt oxide reduction, the lowest amount of platinum is preferable to prepare the catalyst for AFTS. Also, the absence of XRD peaks for cobalt titanate in any of the catalysts even after reduction as well as any high-temperature peak for either cobalt-titanate oxide spinels, indicates that this synthesis process could be highly reliable to prepare the cobalt-supported catalyst, which may prevent the formation of the significant amount of mixed metal oxide during synthesis and reduction step. It makes the catalyst more active and durable for CO hydrogenation by providing more active sites.

3.1.5. TEM analysis:

The TEM images for freshly prepared calcined TiO₂, 1P25C, and 3M1P25C catalysts are shown in Fig. 5 along with their particle size distribution for which > 100 particles were considered, showing that all the particles are below 10 nm. The TEM images for TiO₂ show that it consists of spherical non-agglomerated nanoparticles and comprises of disordered but highly mesoporous structure. The d-spacing of TiO₂ particles is calculated, and it shows 0.351 nm for most of the particles, which correspond to the (1 0 1) phase of anatase TiO₂, and it can be correlated with the most intense peak in the XRD results. The mesoporous structure becomes more intact and ordered after incorporating metals, visible in HRTEM images for 1P25C. The increase in the pore diameter after metals deposition in TiO₂ can be identified from HRTEM images, concomitant with pore size distribution evaluated using the BJH method. The d-spacing of 0.461 nm was observed for cobalt particles related to the CoO₂ phase of cobalt, whereas the d-spacing of 0.217 nm is associated with the MnO phase of manganese. No platinum particle was observed in the TEM images, which may be due to low loadings and high dispersion on the support. Moreover, due to the minimal difference in the mass of Co and Mn, it was not possible to differentiate between Co and Mn from the available TEM images. So, the average particle size distribution for TiO₂ particles is estimated to be in the range of 4.5–7 nm (see Fig. 5a), while the range of particles size distribution for 1P25C (involve Ti and Co) and for 3M1P25C catalyst (involve Ti, Co as well as Mn), it is in the range of 6–8.5 nm. The EDX mapping of 3M1P25C in Fig. S2 shows that all the deposited metal particles are highly dispersed on the TiO₂ matrix.

![Fig. 4. H₂-TPR profile of (a) 1PzCo, (b) xM1P25C, and (c) 3MyP25C catalysts.](image-url)
200nm
200nm
200nm
200nm
0.351nm
6.0 6.5 7.0
0.461nm
TiO2 (101)
0.461nm
TiO2 (101)
0.217nm
MnO (200)
0.217nm
MnO (200)
0.351nm
TiO2 (101)
6.0 6.5 7.0 7.5 8.0 8.5
Particle size (nm )
6.0 6.5 7.0 7.5 8.0 8.5
Particle size (nm )
6.0 6.5 7.0 7.5 8.0 8.5
Particle size (nm )
f)e) d) 
(e - f) 3M1P25C catalysts.

3.1.6. STEM-EDS studies

The STEM-EDS image for the 3M1P25C catalyst is given in Fig. 6, where three highly dispersed colors denote three different elements (Ti = red, Co = blue, Mn = green). The purple (red + blue) colored particles are probably formed by mixing cobalt and titania particles. It might be possible that the cobalt is sitting directly on top of the titania surface. The close association of Mn (MnO) and Co (CoO) is very high [46]. However, it can’t be ruled out that some of the Mn particles are also spread over the surface of titania. Still, most MnO is associated closely with Co3O4 sites, which significantly affect the catalytic activity. The comprehensive study of the interaction of MnO particles with the support and their exact coordination with Co and Ti particles will be inscribed in future publications.

3.1.7. H2 chemisorption studies:

The H2 uptake results and the calculated dispersions of all the catalysts are depicted in Table 4. These results show the enhancement in the percentage reduction with increasing cobalt loading due to the increasing average cluster size of cobalt and the resulting loss of interaction with support. However, the fraction of 30 wt% cobalt on TiO2 further decreases due to its large cluster size, where the only outer layer of cobalt particles absorbs hydrogen. In contrast, the inner particles might remain unreduced. By adding 1.5 and 3 wt% manganese on 1P25C catalyst, the H2 uptake increases with enhanced cobalt dispersion, which is in line with the results reported by Morales et al. [60]. The manganese can react with cobalt during their simultaneous addition while preparing the catalyst and forming Co3+Mn4O4, which may break during reduction. It results in dispersed and small Co particles where MnO might be associated with reduced Co0 particles [60,62]. The increased H2 uptake in the MnO promoted catalysts (1.5 wt% and 3 wt% loading of Mn) could be due to reduced interaction of Co particles with TiO2. The MnO also spreads over the surface of TiO2 during reduction and prevents the interaction of Co with TiO2 up to some extents, which results into comparatively high H2 uptake (Table 4). The addition of higher amounts of manganese lowers the H2 uptake possibly resulting from the masking of cobalt surface sites by MnO.

3.1.8. CO temperature programmed reduction (CO-TPD) studies:

Different CO desorption peaks are observed for Mn-promoted catalysts in the CO-TPD plot (see Fig. 7). The first two chemisorbed peaks appear near 450–600 K and 600–670 K, while the higher temperature peak appears at 730–900 K with the maximum intensity in the case of the 12M1P25C catalyst. Based on previously reported studies [63], the low-temperature desorption peak can be assigned to the linearly adsorbed CO at high CO surface coverages. In contrast, the high-temperature peaks correspond to the CO adsorbed in contact with the MnO promoter. Strongly adsorbed CO will be desorbed at a higher temperature. The high peak intensity at higher temperatures (>600 K) can be correlated to the strong Lewis acid-base interaction between CO and MnO near the cobalt sites. However, the stronger adsorption of CO due to high Mn concentration in the 12M1P25C catalyst was observed. As a result, a fraction of the CO pool is found to increase at high temperature when the loading of Mn was increased from 1.5 wt% to 12 wt%, indicate a more significant number of interacting and active sites for CO by increasing the loading of the promotor. However, this result is in
they observed that chemisorption-uptake analysis by the catalyst with contrast to the previously reported study by Johnson et al. [41], where

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H₂ uptake (µmol/g cat)</th>
<th>O₂ uptake (µmol/g cat)</th>
<th>Fraction reduced</th>
<th>Dispersion</th>
<th>Activity * (molCo₂, molCo⁻¹.h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1P15C</td>
<td>129.9</td>
<td>601.3</td>
<td>35.4</td>
<td>28.8</td>
<td>0.60</td>
</tr>
<tr>
<td>1P20C</td>
<td>119.1</td>
<td>876.7</td>
<td>38.7</td>
<td>18.1</td>
<td>0.93</td>
</tr>
<tr>
<td>1P25C</td>
<td>104.1</td>
<td>1237.3</td>
<td>43.7</td>
<td>11.2</td>
<td>1.44</td>
</tr>
<tr>
<td>1P30C</td>
<td>93.0</td>
<td>1311.5</td>
<td>38.6</td>
<td>9.5</td>
<td>1.94</td>
</tr>
<tr>
<td>1.5M1P25C</td>
<td>114.7</td>
<td>1125.5</td>
<td>39.8</td>
<td>13.6</td>
<td>1.65</td>
</tr>
<tr>
<td>3M1P25C</td>
<td>104.1</td>
<td>979.8</td>
<td>34.6</td>
<td>14.2</td>
<td>1.93</td>
</tr>
<tr>
<td>6M1P25C</td>
<td>99.2</td>
<td>845.4</td>
<td>29.9</td>
<td>15.5</td>
<td>2.00</td>
</tr>
<tr>
<td>12M1P25C</td>
<td>95.8</td>
<td>774.1</td>
<td>27.4</td>
<td>16.5</td>
<td>1.90</td>
</tr>
<tr>
<td>3 M0.25P25C</td>
<td>98.4</td>
<td>834.8</td>
<td>29.5</td>
<td>15.7</td>
<td>1.62</td>
</tr>
<tr>
<td>3 M0.5P25C</td>
<td>89.4</td>
<td>744.4</td>
<td>26.3</td>
<td>16.0</td>
<td>1.75</td>
</tr>
<tr>
<td>1P30C</td>
<td>93.0</td>
<td>1311.5</td>
<td>38.6</td>
<td>9.5</td>
<td>1.94</td>
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<tr>
<td>1P25C</td>
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<tr>
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<td>35.4</td>
<td>28.8</td>
<td>0.60</td>
</tr>
</tbody>
</table>

* H₂ uptake (H₂ desorbed/g cat).

*Reaction conditions: 453 K, 3 MPa, 40 mL water and CO: H₂: N₂ = 1:2:1/3; calculated by excluding CO₂.

Table 4: Results from H₂-TPD and oxygen pulse reoxidation.

The catalytic activity and the product selectivity at various compositions of cobalt, manganese, and platinum were obtained by carrying out the reaction in a batch aqueous phase reactor for 20 h at 453 K temperature and 3 MPa pressure of reaction gas mixture (CO: H₂: N₂ = 1:2:1/3). The respective data is presented in Fig. 8.

3.2. Catalyst activity

The catalytic activity and the product selectivity at various compositions of cobalt, manganese, and platinum were obtained by carrying out the reaction in a batch aqueous phase reactor for 20 h at 453 K temperature and 3 MPa pressure of reaction gas mixture (CO: H₂: N₂ = 1:2:1/3). The respective data is presented in Fig. 8.

3.2.1. The effect of cobalt loading:

The effect of cobalt loading is studied at 453 K by loading 15 wt% (1P15C), 20 wt% (1P20C), 25 wt% (1P25C) and 30 wt% (1P30C) of cobalt (see Fig. 8a), while maintaining 1 wt% platinum loading on TiO₂. The catalytic activity in each case is calculated, excluding CO₂. The results (see Fig. 8a) show that increasing the metal loading increases the CO conversion rate from 0.60 to 1.94 molCo₂/molCo⁻¹.h⁻¹. Ideally, the number of active Co⁶⁺ sites determines the activity of the reduced Co catalysts, where both the quantities are directly proportional to each other. Here, the catalytic activity obtained with increasing the cobalt loading reflects the inverse trend with cobalt dispersion on support and a nonlinear trend with the degree of reduction/ H₂ consumption.

The presence of water in the reaction medium plays a significant role in catalytic activity. These cobalt-based materials show high selectivity for the formation of CO₂ in the aqueous medium under Fischer Tropsch reaction conditions. Interestingly, the selectivity to CO₂ decreases with increasing cobalt content, and the CO₂ yield varies in the small range (18–23%). Although the metallic cobalt is not a water–gas shift active metal, the conversion of CO to CO₂ implies that Co⁷⁺ may become active for a water–gas shift reaction under the presence of water. Increasing the cobalt loading from 15 wt% to 25 wt% increase the C₅₆ selectivity to 58% with 3% methane and 32% CO₂ selectivity.

However, in the 1P30C catalyst, the selectivity for methane further raised to 33%, which can be the consequence of high CO conversion (73%) and CO₂ formation. The conversion of CO to CO₂ results in the increase of H₂ partial pressure (WGSR), and low CO-partial pressure creates an imbalance between the reactant molecules and possibly increases the local H₂: CO ratio around Co(0) sites and leads to methane formation [64]. So, the catalyst with 25 wt% Co on TiO₂ with 1 wt% Pt (1P25C) presents a reasonable degree of reduction as predicted from its reduced fraction, leading to the highest selectivity towards C₅₆, hydrocarbons among all the catalysts.

3.2.1.1. The effect of manganese loading: After optimizing the cobalt loading on TiO₂, our target is to increase the catalytic activity for CO conversion and selectivity of higher hydrocarbon at the expense of CH₄. Manganese, which has been reported to alter the FTS catalytic activity, varied from 1.5 wt% to 12 wt% to check its effect in AFTS (see Fig. 8c) [60,61]. The addition of manganese to the 1 wt% Pt and 25 wt% Co-loaded TiO₂ catalyst increased the CO conversion rate up to a manganese promotion level of 6 wt% (6M1P25C), followed by a slight dip for the 12M1P25C catalyst. The selectivity to C₅₆ hydrocarbons rises to 70% for 3M1P25C and decreases further with increasing Mn loading. The selectivity of CH₄ and lower hydrocarbons (<C₅₆) also increases at the expense of C₅₆ hydrocarbons for 6M1P25C and 12M1P25C. As reported by Johnson et al. [41], the cleavage of the C-O bond is facilitated by the presence of Mn²⁺ cation in a Lewis acid-base interaction, thus increases the rate.

The results obtained from CO-TPD also reveal that with increasing the loading of Mn, the adsorption of CO on the Co sites increases, likely due to the promoting effect of MnO located nearby to the Co sites. However, it has been reported in previous studies that an excess amount of Mn could block the surface of Co particles, decreasing the activity by a more significant difference [61,65]. However, our observation showed a slight decrease in CO conversion rate from 2.0 to 1.90 molCo₂/molCo⁻¹.h⁻¹ from 6M1P25C to 12M1P25C, respectively. It implies that a high amount of Mn and Co on TiO₂ can also favor high catalytic activity. The mentioned loading of promoter (12 wt%) with Co over TiO₂ becomes highly selective for olefins, which can be another study.
The surface compositions obtained from XPS studies (see Table S3) also show that the surface becomes rich by Co and Mn with increasing Mn loading. The TPR results found that the low amount of manganese shifts the peak maxima to the lower value. The addition of Mn also shows that the surface becomes rich by Co and Mn with increasing Mn loading. The TPR results found that the low amount of manganese on cobalt and platinum-loaded TiO$_2$ increases the dispersion of cobalt particles over the surface of TiO$_2$, which can be the reason for its enhanced CO conversion rate. However, high dispersion also leads to small cobalt particles, which are prone to strong SMSI’s and thus are harder to reduce. The low reduced fraction in the catalysts with more manganese was also found through chemisorption studies.

Consequently, CoO particles also favor the water gas shift reaction that produces CO$_2$ and H$_2$, followed by the formation of CH$_4$ and lower hydrocarbons. However, there are no reports on the promotional effect of manganese on cobalt and platinum-loaded TiO$_2$ in AFTS. The above studies concluded that the 3M1P25C catalyst shows an excellent catalytic activity while showing the C$_5$ selectivity up to 64%.

3.3. Reaction study

The catalytic studies were carried out in a batch aqueous phase reactor over 20 h at temperatures between 433 K and 473 K and pressures between 2 and 3 MPa with 0.5 g catalyst. The effect of process conditions (time, temperature, and pressure) on selected catalyst performance is shown in Fig. 9.

3.3.1. Reaction time

Fig. 9a shows the effect of time in the reactor on the CO conversion and selectivity towards CO$_2$, CH$_4$, C$_2$H$_4$, and C$_5$ for 3M1P25C. Kinetics and selectivity studies within batch phase reactors for the Fischer-Tropsch synthesis are scarce [4] due to changes in the partial pressures, conversions, and overall reaction pressure with time, making the system inherently complex.

Increasing the reaction time from 1 h to 5 h, 10 h, 15 h, and 20 h resulted in an increase in CO conversion from 9% to 27%, 44%, 61%, and 70%. At a reaction time of 1 h, the CO$_2$ selectivity was 13.6C-%, which increased slightly to 20.1C-% at 5 h and then decreased to 11C-% after 20 h. The selectivity towards CO$_2$ is elevated compared to typical cobalt-based Fischer-Tropsch studies in a CSTR or fixed bed reactor [64,67,68]. It may be due to excess water in the reaction system, which facilitates the water-gas shift reaction. However, it is also possible that this is a factor of the batch reactor system itself. High CO$_2$ selectivity (10–14C-%) was reported by Lu et al. [4] for a cobalt catalyst within a non-aqueous batch reactor system.

The methane selectivity over 1–20 h ranged from 0.63C-% to 7.89C-%, which is relatively low compared to similar Fischer-Tropsch batch systems using cobalt-based catalysts [4]. It is likely indicative of the positive effect that manganese promotion has on lowering methane selectivities when added in small quantities [63,69], as well as the low reaction temperature (453 K) and high pressure (3 MPa) concerning slurry-bed low-temperature Fischer-Tropsch, which is typically carried...
The CO conversion increased from 27.5% to 91.9% over the 40 K temperature rise. At the lower temperatures of 433 K and 453 K, the CH4 selectivity remained low between 3 and 6C-% while the CO2 selectivity was high, between 31 and 32C-%. Increasing the temperature further to 473 K led to a substantial increase in CH4 and a decrease in CO2. Methanation is kinetically enhanced by higher temperatures, while high conversions (91.9%) enhance CH4 formation in well-mixed reactors due to higher H2/CO ratios [64]. The decrease in CO2 may be due to thermodynamic limitations at higher temperatures (the water–gas shift reaction is exothermic). The significant increase in CH4 formation at 473 K led to a decrease in the selectivity towards C5+, hydrocarbons.

It is found that the catalytic activity increases steadily with increasing temperature. The reaction rate is found to be 0.76 molCO/molCo⋅h at 433 K while changing the temperature to 473 K; the rate is raised to 2.62 molCO/molCo⋅h. The CO coverage and temperature are reported to be inversely proportional to each other. The rate of CO dissociation is firmly dependent on surface topology, temperature, and CO coverage. The CO coverage appears to be high at low temperatures, resulting in the low dissociation of CO due to changes in the number of mols over the Fischer-Tropsch reaction.

3.3.2. Reaction temperature

The influence of reaction temperature for AFTS was studied using the 1P25C catalyst for temperatures between 433 K and 473 K. The change in the conversion, selectivity, and activity during AFTS at different temperatures for 1P25C catalyst is shown in Fig. 9b and Fig. 8b.

The CO conversion increased from 27.5% to 91.9% over the 40 K temperature rise. At the lower temperatures of 433 K and 453 K, the CH4 selectivity remained low between 3 and 6C-% while the CO2 selectivity was high, between 31 and 32C-%. Increasing the temperature further to 473 K led to a substantial increase in CH4 and a decrease in CO2. Methanation is kinetically enhanced by higher temperatures, while high conversions (91.9%) enhance CH4 formation in well-mixed reactors due to higher H2/CO ratios [64]. The decrease in CO2 may be due to thermodynamic limitations at higher temperatures (the water–gas shift reaction is exothermic). The significant increase in CH4 formation at 473 K led to a decrease in the selectivity towards C5+, hydrocarbons.

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The increase in reaction pressure from 2 MPa to 3 MPa led to a substantial decrease in CH4 and CO2 selectivities, likely due to enhanced chain growth probabilities at high pressures and a thermodynamic favorability towards the Fischer-Tropsch products over the water–gas shift reaction. The low selectivities towards CO2 and CH4 led to high C5+, selectivity at 3 MPa of 73C-%. There was an opposite effect on the further increase of the pressure with a substantial increase in CO2 and CH4 and a decrease in C5+, selectivity. It is not likely due to the pressure itself, but rather the high CO conversion (93%) which shifts the Fischer-Tropsch synthesis into an unfavorable regime (for well-mixed reactors), where CH4 partial pressures and H2/CO ratios are high, resulting in enhanced methanation and water–gas shift activities [64].

3.3.3. Reactor pressure

Fig. 9c shows the effect of reaction pressure (initial pressure in the aqueous phase batch reactor) on the conversion and selectivity for 3M1P25C. The increase in reaction pressure from 2 MPa to 4 MPa bar had a significant effect on the conversion of CO, which increased from 49% to 93%. Fischer-Tropsch reaction rates are inherently linked to the partial pressures of reactants CO and H2, which increase proportionally to the overall reaction pressure.

The increase in reaction pressure from 2 MPa to 3 MPa led to a substantial decrease in CH4 and CO2 selectivities, likely due to enhanced chain growth probabilities at high pressures and a thermodynamic favorability towards the Fischer-Tropsch products over the water–gas shift reaction. The low selectivities towards CO2 and CH4 led to high C5+, selectivity at 3 MPa of 73C-%. There was an opposite effect on the further increase of the pressure with a substantial increase in CO2 and CH4 and a decrease in C5+, selectivity. It is not likely due to the pressure itself, but rather the high CO conversion (93%) which shifts the Fischer-Tropsch synthesis into an unfavorable regime (for well-mixed reactors), where CH4 partial pressures and H2/CO ratios are high, resulting in enhanced methanation and water–gas shift activities [64].

3.3.4. Kinetic analysis

While many empirical macro-kinetic expressions [4–10] exist (see Table 5) to describe the rate of cobalt-based Fischer-Tropsch systems, these are typically derived using flow reactors (slurry or fixed bed). Developing an empirical rate expression for an aqueous batch reactor system is non-trivial due to changes in partial pressures and rates with respect to time. In a batch reactor, as the reaction progresses with time, reactants CO and H2 are converted to products H2O and hydrocarbons (see Fig. S3). This increases conversion, a decrease in the partial pressures of CO and H2, which will inherently decrease the rate of hydrocarbons formation [11] over time. The batch reactor in this study is also non-isobaric, meaning that the overall pressure in the reactor decreases due to changes in the number of mols over the Fischer-Tropsch reaction. Figure S3 shows the change in the partial pressure of reactants and products in an aqueous phase batch reactor based on reaction stoichiometry and experimental CO conversions over 20 h for 3M1P25C.

Using a least-squares regression of the experimentally derived reaction rates as a function of time for 3M1P25C (derived as per section 2.4) and the partial pressures shown in Fig. S3, the constants for various empirical rate laws were derived (see Table 5).

Fig. 10 shows a comparison between the empirical rate laws (with constants in Table 5) and experimental data. The experimental rate of CO consumption decreases with an increase in CO conversion, as
predicted by all of the empirical rate expressions used in this study [34–37,70], due simply to the decrease in the partial pressure of reactants at higher conversions. There is a slight deviation from the empirical models at higher conversions (and thus reaction times). This indicates no strong deactivation of the catalyst between reaction time 1 h and 12 h.

Despite being run in batch operation, 3M1P25C is modeled well by all five empirical rate laws. The model by Li et al. [36] is derived with water as a contributing factor to the rate. However, the constants derived with least squares regression for 3M1P25C in an aqueous phase reactor is zero for the partial water pressure term. It indicates very little dependence on the partial pressure of water for the rate of reaction in this case. On the other hand, the kinetic model by Ma et al. [34], which also has water as a contributing partial pressure to the rate, was found to have a significant constant, which affects the fit at higher conversions, albeit this may be due to the contribution from the hydrogen term.

### 4. Conclusion

In conclusion, this work demonstrates a facile synthesis method for controlled and uniform-sized cobalt and titania nanoparticles, which are highly efficient for aqueous phase FT synthesis. The aqueous phase Fischer-Tropsch synthesis is highly efficient at low temperatures (less than 473 K), whereas high temperatures favor CH₄ formation and light hydrocarbons. The optimized catalysts with a composition of 25 wt% Co, 3 wt% Mn and 0.5 wt% Pt and exhibited a CO conversion at a rate of 1.75 molCO/molCo.h⁻¹, a 73C-% C₅⁺ selectivity, and less than 5% methane formation. The presence of platinum significantly improves the reducibility of cobalt-oxide. Moreover, the addition of Mn enhanced the Lewis-acid base interaction between O atom of CO and Mn²⁺ lies at the interface between Co-MnO sites, confirmed by the combined result obtained from STEM image and enhanced CO adsorption and hence improves the catalytic activity considerably. Moreover, the CO conversion rates were modeled well by standard Fischer-Tropsch empirical rate laws for cobalt-based catalysts with little H₂O term dependence. The

### Table 5

Empirical kinetic models and corresponding constants derived using least squares regression for 3M1P25C at 300 K, 3 MPa with 0.5 g catalyst [34–37,71]

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>a¹</th>
<th>b²</th>
<th>c</th>
<th>d</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sarup &amp; Wojciechowski (1989)</td>
<td>0.52</td>
<td>0.21</td>
<td>0.000010</td>
<td>0</td>
<td>[70]</td>
</tr>
<tr>
<td>Yates &amp; Satterfield (1991)</td>
<td>0.33</td>
<td>0.41</td>
<td>–</td>
<td>–</td>
<td>[37]</td>
</tr>
<tr>
<td>Li et al. (2002)</td>
<td>0.45</td>
<td>0</td>
<td>0.37</td>
<td>0.31</td>
<td>[36]</td>
</tr>
<tr>
<td>Botes et al. (2009)</td>
<td>0.74</td>
<td>0.59</td>
<td>–</td>
<td>–</td>
<td>[35]</td>
</tr>
<tr>
<td>Ma et al. (2014)</td>
<td>0.39</td>
<td>0.14</td>
<td>–</td>
<td>–</td>
<td>[34]</td>
</tr>
</tbody>
</table>

¹mol CO/molCo.h.  
²bar⁻¹.

Fig. 10. Comparison between empirical kinetic models (with constants derived by least-squares regression) and rates of CO consumption for 3M1P25C in an aqueous batch phase reactor.
reported catalyst system is very effective for synthesizing C_{15} hydrocarbons in a single step.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2021.122402.

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Further reading