Synthesis and characterization of perovskite-supported CoNi catalyst for CO oxidation via exsolution

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Abstract. The introduction of perovskite oxide as catalysts alternative has increased the worldwide interest due to its advantages such as its versatility to accommodate different transition metals. This study set out to evaluate the catalytic activity of CO oxidative perovskite catalysts (LCCNTO), fabricated via solid-state method and reduced under various reducing condition for the exsolution of the active metals, Cobalt-Nickel (CoNi) from the perovskite lattice. The effect of reducing parameter modification towards the catalytic activity of the fabricated LCCNTO was discussed in terms of CO conversion and CO₂ production rate.

Through the light-off test, the sample that reduced with the longest deration (S2T10H6-R5H5) showed the highest CO conversion of 45.45% and CO₂ production rate of 0.1409 x 10⁻⁴ mol s⁻¹ g⁻¹ at the reaction temperature of 500 °C. Not only that, it was discovered that by controlling the reducing duration, the initiate temperature for the reaction to occur was lowered from 360 °C (S2T10H6-R5H3) enabling the reaction to occur at lower temperature at 280 °C in S2T10H6-R5H5. Under the same reducing temperature, the CO₂ production of sample reduced for 200 minutes (S2T10H6-R5H3) started at 360 °C but as the reducing duration increased to 300 minutes (S2T10H6-R5H5), the CO oxidation initiated at a much lower temperature of 280 °C. Although LCCNTO catalyst still suffer from similar deterioration as the other reported base metal catalyst, but tuning the reducing duration given to a sample, it greatly affects the initiation temperature for the reaction to occur.

1. Introduction
The increasing uses of fossil fuel and motor vehicles had brought the rise in air pollution with their high production of exhaust emission and carbon monoxide (CO) being one of the major atmospheric pollutant emitted from incomplete combustion of carbon source fuel poses a serious threat to human health [1]. Hence the use of oxidative catalyst system is crucial for the removal of exhaust gases such as CO by converting them into a less hazardous gases, carbon dioxide (CO₂) [2]. Supported heterogeneous oxidative catalysts usually consist of high catalytic active metals being uniformly scattered onto the surface of a porous support material which typically fabricated through deposition
or precipitation method. Although deposition method has been widely applied in heterogeneous catalyst fabrication but the active metals deposited onto the surface have limited anchorage to the supporting material. Not only they have minimal control over the particle distribution and size during both preparation and catalyst activation stages [3], but also known to be time-consuming and costly [4].

The discovery of the unique structural properties of perovskite oxide which capable of accommodate various base metals and elevating them from within its supporting structure through exsolution process had caught the attention to be a befitting support material for heterogenous catalyst [5]. With the nominal composition of ABO$_3$, perovskite can couple up two cations, A and B where alkali earth metals with larger ionic radius occupy the A site while B site cations, being a much smaller ionic radius metal can be substituted with different high catalytic elements. Since 90% of the elements in the periodic table could be stable in the perovskite structure, the application of perovskite oxides could be further broadened with partial substitutions of secondary cations (A' and B') to form A$_{1-x}$A'B$_{1-y}$B'O$_3$ [6]. The different sizes of the elements substituted into the perovskite system can cause various degree of structural distortion due to their ionic radii differences in the lattice and deviate from the ideal cubical structure of perovskite. In order for the perovskite oxide with all the substituted formulation to be stable, Goldschmidt’s tolerance factor, t is calculated by using the ionic radii of the perovskite structure and the value 0.75 to 1 is required [7]. Figure 1 depicted a simplified illustration of exsolution process.

![Exsolved (CoNi) nanoparticles](image)

**Figure 1.** Simplified illustration of exsolution process for Co doped perovskite.

In the place of the high scarcity precious metals such as Pt, Rh, Pd and Au, a lower cost with higher stability substitution is require to fill the uprising demands of oxidative catalyst. Transition metals fits the requirement and deemed to be a more environmentally friendly alternative as heterogeneous catalyst for both their relative affordability and their effective surface redox reactivity [9, 10]. Among the candidates, cobalt oxide and nickel oxide showed their potential in CO oxidation where cobalt oxide had shown impressive reactivity towards CO oxidation at low temperatures [10] and nickel oxide demonstrated astounding catalytic activity in both CO and NO removal [12, 13]. Since both Co and Ni have similar electronic configurations, Co-Ni composite oxides are capable of exhibit synergistic catalytic effects [13] and have a strong adsorption capacity of CO that work splendidly at low temperatures [14].

With the uniqueness of perovskite oxide’s structure being a suitable porous supporting material for heterogeneous catalyst, CoNi was chosen as our CO oxidative active metals and were incorporated
into the perovskite formulation, LCCNTO to act as a cost-effective alternative. Solid-state reaction was used to fabricate LCCNTO and the active metal CoNi had successfully exsolved onto the surface of LCCNTO for CO oxidation. The structure of LCCNTO along with the single metal system LCCTO and LCNTO were characterized using X-ray diffraction (XRD) to determine their average crystallite size and identify their perovskite structure. The catalytic activity of the fabricated LCCNTO was evaluated in terms of CO conversion and the CO$_2$ production rate, $r^*_{CO_2}$, obtained from light-off experiments to determine the effects of different reducing duration on the catalytic activity of the samples towards the oxidation of CO.

2. Materials and methods

2.1. Chemical and gases

99.5% Cobalt (III) oxide (Co$_3$O$_4$) was purchased from Sigma-Aldrich, United States, while other precursors such as 99% Nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$$\cdot$6H$_2$O), 99.9% Ceria oxide (CeO$_2$), 99.98% Lanthanum oxide (La$_2$O$_3$), and Titanium oxide (TiO$_2$) were purchased from Acros Organics, United States. While the gases used include 30% hydrogen/argon (H$_2$/Ar) and 99.999% nitrogen (N$_2$) for the reduction process while 20% oxygen/nitrogen (O$_2$/N$_2$) and 20% carbon monoxide/nitrogen (CO/N$_2$) were used in CO oxidation during light-off test. All the gases mentioned were purchased from Linde group, Ireland. All chemicals and gases for experimental works were used without additional purification.

2.2. Sample preparation

The composite CoNi, Co and Ni incorporated oxidative perovskite catalysts, LCCNTO (La$_{0.7}$Ce$_{0.1}$Co$_{0.3}$Ni$_{0.1}$Ti$_{0.6}$O$_3$), LCCTO (La$_{0.7}$Ce$_{0.1}$Co$_{0.4}$Ti$_{0.6}$O$_3$) and LCNTO (La$_{0.7}$Ce$_{0.1}$Ni$_{0.4}$Ti$_{0.6}$O$_3$) were fabricated through solid-state reaction which involved the fabrication of perovskite structure through calcination of precisely weighed and well mixed precursors, La$_2$O$_3$, CeO$_2$, Co$_3$O$_4$, Ni(NO$_3$)$_2$$\cdot$6H$_2$O and TiO$_2$. The mixed precursors were first heated to remove any moisture and volatile substance prior to a calcination process for 12 hours at 1000 °C to produce pure perovskite structure. In order for the metal particles to be exsolved onto the surface, the LCCNTO samples were exposed to a reducing environment with hydrogen gas (H$_2$) as the reducing agent in a conventional continuous flow reactor at different reducing duration to determine the effect of reducing duration on the catalytic activity of these fabricated LCCNTO.

Both the exsolution and CO oxidation were carried out in a conventional continuous flow reactor consisted of a quartz fixed-packed bed reactor with gases supply connected with mass flow controller (MFC). As-prepared LCCNTO were held in position with two supporting quartz wool to remain at the centre of the heating element prior to the exsolution and CO oxidation. Figure 2 depicted the simplified experimental set-up of the conventional continuous flow reactor. According to the fabrication method mentioned in Wan Ramli et al. [15], the reducing temperature between 550 to 860 °C is the suitable range for CoNi exsolution and have direct influence on the particles’ size of exsolved CoNi on the perovskite. The exsolved CoNi particles’ size reported around 30 nm when reduced at 860 °C but the size of exsolved particles reported to be 10 nm when reduced at around 500 °C, but 10 nm particles size was too small for activation when exposed to CO-rich environment but 30 nm was too big causing agglomeration of particles during the activation. With all their samples were reduced for 5 hours, in order to further investigate the effects of reducing parameter towards the degree of exsolution, reducing temperature of 500 °C and 700 °C with different the reducing duration were chosen to determine the effects of reducing parameters on degree exsolution of CoNi from LCCNTO. The exsolution was done under different reducing condition with a continuous H$_2$ supply at 20 ml min$^{-1}$ and the reducing condition was as listed in table 1.
Figure 2. Experimental set up for the exsolution and light-off test.

Table 1. LCCNTO samples with their treatment stages and conditions.

| Sample            | Stage                      | Conditions                          |
|-------------------|----------------------------|-------------------------------------|
| $S_2T_{10}H_6$    | Secondary Calcination      | $T = 1000\, ^\circ\text{C}$, calcined for 360 minutes |
| $S_2T_{10}H_6-R_3H_3$ | Reduction Process         | $T = 500\, ^\circ\text{C}$, reduced for 200 minutes         |
| $S_2T_{10}H_6-R_4H_4$ |                         | $T = 500\, ^\circ\text{C}$, reduced for 250 minutes         |
| $S_2T_{10}H_6-R_5H_5$ |                         | $T = 500\, ^\circ\text{C}$, reduced for 300 minutes         |
| $S_2T_{10}H_6-R_7H_5$ |                         | $T = 700\, ^\circ\text{C}$, reduced for 300 minutes         |

2.3. Sample characterisation

The crystalline structures of the fabricated samples were analysed using Bruker D2 Phaser benchtop X-ray diffractometer (XRD), equipped with LYNEYE 1D Ultra-fast-solid-state detector with CuKα radiation ($\lambda = 1.54184$ Å) to ensure the formation of the desired perovskite structures. LCCTO and LCNTO were fabricated along with LCCNTO to observe the change in structure and average crystallite grain size. The average crystallite grain size of the as-prepared catalysts was estimated by using the major peaks presence from the XRD pattern using Scherrer equation:

$$d = \frac{K\lambda}{\beta \cos \theta}$$

where $d$ is the is the crystallites size (nm), $K$ represent the Scherrer constant of 0.9, $\lambda$ depends on the wavelength of the x-ray source ($\lambda = 1.54184$ Å), $\beta$ is the full width at half maximum (FWHM) in radians and $\theta$ denote the peak positions in radians.

2.4. Catalytic activity testing

The catalytic activities of reduced LCCNTO ($S_2T_{10}H_6-R_3H_3$) were tested using the same reactor set up shown in figure 2. The catalyst powder was first diluted with $\text{Al}_2\text{O}_3$ powder down to 10 wt% to have a reasonable pressure drop within the reactor [15]. The inlet gases supply to the catalytic testing performed was set according to the stoichiometric reaction of CO oxidation as shown as follow:

$$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$$

(2)
The total inlet feed gas mixture of 2% CO and 1% O$_2$ gases, balanced with N$_2$ gas with the total flowrate $F_t = 250$ ml min$^{-1}$ given at normal temperatures. The activity of all the reduced catalyst as a function of temperature or also known as the light-off test, was conducted to determine the effectiveness of the catalyst toward CO oxidation with IR analyzer (Testo 340, Germany) to record the CO$_2$ production at different temperature. In this study, the light-off test was set to obtain the data from room temperature to 520 °C, with a step size of 20 °C. The temperature was held constant at every temperature increment for 40 minutes for the reaction to take place, and also to obtain stable values of CO$_2$ produced. The CO conversion and reaction rates, $r^\ast_{CO_2}$, in terms of CO$_2$ production for all samples were calculated as follow:

$$CO \; conversion, \% = \frac{CO_2 \; produced \; (ppm)}{Total \; CO \; supply \; (ppm)} \times 100\%$$  \hspace{1cm} (3)$$

$$r^\ast_{CO_2}(mol \; (CO_2)s^{-1}g^{-1}) = \frac{y_{CO_2}xh}{w_p}$$ \hspace{1cm} (4)$$

where $y_{CO_2}$ is the CO$_2$ concentration (ppm) measured by the analyzer at the gas outlet, $n$ is the total molar flow rate of the reaction and $w_p$ is the weight of the active catalysts ($w_p = 60$ mg).

3. Results and discussion

3.1. X-ray diffraction investigation

The analysis of X-ray diffraction pattern consisted of LCCNTO (CoNi), LCCTO (Co) and LCNTO (Ni) was performed to determine the difference in the structure of fabricated perovskite with different active metal. All the samples exhibited the formation of perovskite phase with peaks labelled as shown in figure 3 [16]. Upon the calcination, the formation of the perovskite structure was favoured in all the samples with the peaks corresponded to perovskite phase could be identified with slight difference in intensity. The peaks for each active metals (Co, Ni and CoNi) were also identified indicating the incorporation of active metals in the perovskite structure [17]. Due to the similar electronic configuration of Co and Ni, several of peaks overlapped with each other and the doped LCCNTO and LCCTO have more similarity with difference in intensity and extra peaks from Ni. The peaks indicating the presence of CoNi are around 2θ = 40° and 58°, but with lower intensity. The average crystallite grain size of prepared samples was calculated using Scherrer equation and the results indicate a decrease in crystallite size with the order of LCNTO (25.1280 nm), LCCNTO (25.0408 nm) and LCCTO (18.1051 nm) which suggested that the doping of cobalt with nickel (3:1) has little to none in reducing the crystallite size of LCCNTO. This was in agreement with the work of Yi and colleagues which reported the increase in Co incorporation of NiO had gradually causing the peaks ascribed to NiO becoming wider and weaker even disappeared when content of Co became higher but at the same time, the Ni$^{2+}$ were suspected to be partially substituted Co$^{3+}$ and move into the Co$_3$O$_4$ crystal lattice forming Ni-Co spinel structure as they both coexist under a same structure [14].
Figure 3. XRD patterns for LCCNTO, LCNT0 and LCCTO with □ denotes the peaks indicating the presence of the perovskite phase while c and n denotes the peaks for both Co and Ni phases, respectively.

3.2. Catalytic activity testing with light-off test

The catalytic activity of fabricated LCCNTO samples (S\textsubscript{2}T\textsubscript{10}H\textsubscript{6}-R\textsubscript{5}H\textsubscript{5}) undergone the light-off test which involved a total flowrate, F\textsubscript{o}, of 250 ml min\textsuperscript{-1} under normal temperature and pressure (NTP) with a continuous inlet flow of 2% CO and 1% O\textsubscript{2} gases balanced with N\textsubscript{2} gas supplied during the oxidation process. Figure 4 compares both the CO conversions and the rate of CO\textsubscript{2} production, \( r^{*}_{\text{CO}_2} \) for samples with different reducing duration. Unreduced LCCNTO sample (S\textsubscript{2}T\textsubscript{10}H\textsubscript{6}) was also tested as a control sample but since no CO\textsubscript{2} produced at the temperature range used, proving that, CO oxidation only occurs to reduced samples with their active metals (CoNi) exsolved onto the surface that were accessible for the reaction. All the catalytic activity of all the samples increased with the reaction temperature where S\textsubscript{2}T\textsubscript{10}H\textsubscript{6}-R\textsubscript{5}H\textsubscript{5} marked the highest CO conversion of 45.45 ± 4.5% which corresponded to the CO\textsubscript{2} production rate, \( r^{*}_{\text{CO}_2} \) of around \( 0.1409 \times 10^{-4} \) mol s\textsuperscript{-1}g\textsuperscript{-1} at the temperature of 500 °C, followed by S\textsubscript{2}T\textsubscript{10}H\textsubscript{6}-R\textsubscript{4}H\textsubscript{4} with the highest CO conversion of 24.46 ± 2.45% and \( r^{*}_{\text{CO}_2} \) of around \( 0.0758 \times 10^{-4} \) mol s\textsuperscript{-1}g\textsuperscript{-1} at 500 °C and lastly S\textsubscript{2}T\textsubscript{10}H\textsubscript{6}-R\textsubscript{3}H\textsubscript{3} with the lowest in both highest CO conversion and achieved at 15.97 ± 1.58% and around \( 0.0495 \times 10^{-4} \) mol s\textsuperscript{-1}g\textsuperscript{-1} at 420 °C, respectively. S\textsubscript{2}T\textsubscript{10}H\textsubscript{6}-R\textsubscript{3}H\textsubscript{3} fabricated exhibited a higher conversion of CO but at much lower CO\textsubscript{2} production rate when compared to the CoNi based exsolved perovskite catalyst reported in Wan Ramli \textit{et al.} \cite{18} with CO conversion rate near 40% but the CO\textsubscript{2} production rate reaching around \( 0.8 \times 10^{-4} \) mol s\textsuperscript{-1}g\textsuperscript{-1} at the temperature of 520 °C with their CoNi exsolved catalyst even before the activation under CO-rich environment.
An interesting trend was observed during the light-off tests in which the initiation temperature for the CO oxidation to initiate becomes lower by increasing the reducing duration of \( S_2T_{10}H_6 \). From the initiation temperature recorded at 360 °C for \( S_2T_{10}H_6 \) that reduced at 500 °C for 200 minutes (\( R_5H_3 \)) to start the reaction, the initiation temperature had lowered to 320 °C by changing the reducing duration of \( S_2T_{10}H_6 \) from 200 minutes to 250 minutes (\( R_5H_4 \)) and the initiation temperature for reaction further dropped as \( S_2T_{10}H_6-R_5H_5 \) was able to start the CO conversion at the temperature of 280 °C. The improvement in terms of the initiation temperature which allow the oxidation process to start at lower temperature might be caused by the better exsolution of CoNi onto the surface with extended reducing duration. It shows a possible new controlling parameter in the future for manipulating the exsolution of active metal in perovskite by tuning the reducing duration.

A drop in catalytic activity was observed upon reaching the highest CO conversion as both the CO conversion and \( r^*_{CO_2} \) started to deteriorate at higher temperature for all samples (\( R_5H_{3.5} \)). It was suspected that the active cobalt alloy undergone surface oxidation during the process and formed other inactive phase which deteriorate the catalytic activity of the catalyst as Co have multiple oxidation state that is not reactive towards CO oxidation [19]. Popovic et al. reported similar phenomenon with their \( La_{0.6}Ca_{0.4}FeO_3-\delta \) catalyst where the CO\(_2\) production increased as the reaction temperature reached 300 °C, a sharp drop was observed, as the temperature continue to increase. It was explained to be caused by the oxygen vacancy and the ion mobility of lattice oxygen that act as the reservoir for CO oxidation enabling the CO conversion rate to increase as the reaction temperature increase until it reaches its equilibrium [20]. All of these can only be a speculation of what happened and will be investigated in future studies.

![Figure 4. CO conversion and CO\(_2\) production rates, \( r^*_{CO_2} \) as a function of temperature (light-off) of the sample \( S_2T_{10}H_6 \) with different reducing duration during exsolution of CoNi from LCCNTO under CO oxidation process. The inlet feed gas consisted of mixture of 2% of CO and 1% of O\(_2\) balanced with \( N_2 \) with total flowrate, \( F_{\text{in}} \), of 250 ml min\(^{-1}\) and GHSV = 23575.45 h\(^{-1}\). Powder weight of 60 mg samples had diluted with alumina to obtain the weight of powder bed, \( W_t \), of 600 mg. Error of around ±10 % were found during reproducibility test at each measured point.](image-url)
A sample of $S_2T_{10}H_{6}$ that reduced at a higher reducing temperature of 700 °C ($R_{10}H_3$), but under the same reduction duration was also prepared to determine the effect of reducing temperature towards the catalytic activity in comparison to $S_2T_{10}H_6$-$R_3H_3$ and the comparison result is as shown in figure 4. The CO oxidation also initiated at the reaction temperature of 280 °C, similar with the initiating temperature of $S_2T_{10}H_6$-$R_3H_3$, but it reached the highest CO conversion of 50 ± 5% and CO$_2$ production rate, $r^*_{CO_2}$ of around 0.1550 x 10$^{-5}$ mol s$^{-1}$g$^{-1}$ at 400 °C, showing a better catalytic activity compared to $S_2T_{10}H_6$-$R_3H_3$, which achieved the highest CO conversion at a higher temperature of 500 °C. However, the conversion started to drop after 400 °C, indicating that $S_2T_{10}H_6$-$R_3H_3$ performs better at lower temperature than $S_2T_{10}H_6$-$R_3H_3$ but less suitable for reaction at higher temperature application. The improvement on CO conversion and CO$_2$ production rate of $S_2T_{10}H_6$-$R_3H_3$ before 400 °C can be attributed to the better exsolution of active metals with higher reducing temperature causing higher weight percentage and larger particles size of exsolved active metal during reduction [16, 22]. As for the drop in catalytic activity after 400 °C, it might be due to possible sintering effect at higher temperature during CO oxidation that deteriorate the active sites of catalyst as active metals exsolved [22] or the degradation of the active phase to a less active phases as surface oxidation of Co might occurred during the reaction [23]. The experiments were repeated to determine the reproducibility of the results and showed an error around 10% for every measured point. Further analysis such as XPS is required to determine the oxidation state of these active metals on the surface and are currently being investigated.

4. Conclusion

LCCNTO oxidative perovskite catalysts were fabricated through solid-state reaction and the structure phase of perovskite were identified using XRD analysis along with its single metal systems; LCCTO and LCNTO. The average crystallite grain size of this fabricated LCCNTO is determined to be around 25.0408 nm and due to the incorporation of Co, the crystalline size was slightly reduced in comparison to the size of its Ni counterpart (LCNTO) of 25.1280 nm. The Co-counterpart, LCCTO exhibited the smallest average crystallite grain size of 18.1051 nm and this has successfully reduced the crystallite size of LCCNTO in which the CoNi particles become smaller and were able to disperse evenly. The exsolution of active metal CoNi was achieved through continuous reduction at 500 °C with various reducing duration ranging from 200 to 300 minutes, ($R_{10}H_3$). With the reducing temperature of 500 °C, reduced LCCNTO ($S_2T_{10}H_6$-$R_3H_3$) exhibited the highest CO conversion of 45.45 ± 4.5% and CO$_2$ production rate of around 0.1409 x 10$^{-4}$ mol s$^{-1}$g$^{-1}$ at 500 °C. A decreasing trend in the initiation temperature for CO oxidation could be observed as the reducing duration for $S_2T_{10}H_6$ increased, where LCCNTO reduced for 200 minutes ($S_2T_{10}H_6$-$R_3H_3$) has its CO conversion started at the temperature of 360 °C but when LCCNTO reduced for 300 minutes ($S_2T_{10}H_6$-$R_3H_3$), the CO conversion start at 280 °C. Similar initiation temperature of 280 °C could be observed when using LCCNTO reduced with same reducing duration of 300 minutes but higher reducing temperature of 700 °C ($S_2T_{10}H_6$-$R_3H_3$) which marked a higher CO conversion of 50 ± 5.0% and CO$_2$ production rate of around 0.1550 x 10$^{-5}$ mol s$^{-1}$g$^{-1}$ at lower temperature of 400°C. Although all LCCNTO suffers from deterioration in the end, but it opens up the possibility of further tuning a better oxidative perovskite catalyst that can functioned at lower temperature.

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References

[1] Duro J A 2016 Intercountry inequality on greenhouse gas emissions and world levels: An
integrated analysis through general distributive sustainability indexes *Ecol. Indic.* **6** 173–9

[2] Park S, Kim Y, Noh Y, Kim T, Han H, Yoon W, Choi J, Yi S H, Lee W J and Kim W B 2019 A sulfur-tolerant cathode catalyst fabricated with in situ exsolved CoNi alloy nanoparticles anchored on a Ruddlesden-Popper support for CO$_2$ electrolysis *J. Mater. Chem. A* **8** 138–48

[3] Lindenthal L, Rameshan R, Summerer H, Ruh T, Popovic J, Nenning A, Löffler S, Opitz A K, Blaha P and Rameshan C 2020 Modifying the surface structure of perovskite-based catalysts by nanoparticle exsolution *Catalysts* **10** 1–14

[4] Neagu D, Tsekouras G, Miller D N, Ménard H and Irvine J T D 2013 In situ growth of nanoparticles through control of non-stoichiometry *Nat. Chem.* **5** 916–23

[5] Tsekouras G, Neagu D and Irvine J T S 2013 Step-change in high temperature steam electrolysis performance of perovskite oxide cathodes with exsolution of B-site dopants *Energy Environ. Sci.* **6** 256–66

[6] Atta N F, Galal A and El-Ads E H 2016 Perovskite nanomaterials – Synthesis, characterization, and applications *Perovskite Materials - Synthesis, Characterisation, Properties, and Applications*, ed L Pan and G Zhu (IntechOpen) chapter 4 pp 107–51

[7] Dragan M, Enache S, Varlam M and Petrov K 2019 Perovskite-type lanthanum cobaltite LaCoO$_3$: aspects of processing route toward practical applications *Co$\text{b}$alt Compounds and Applications*, ed Y Yildiz and A Manzak (London: IntechOpen) chapter 6

[8] Faure B and Alphonse P 2016 Co – Mn-oxide spinel catalysts for CO and propane oxidation at mild temperature *Appl. Catal. B Environ.* **180** 716–25

[9] Petitto S C, Marsh E M, Carson G A and Langell M A 2008 Cobalt oxide surface chemistry: the interaction of CoO(1 0 0), Co$_3$O$_4$(1 1 0) and Co$_3$O$_4$(1 1 1) with oxygen and water *J. Mol. Catal. A Chem.* **281** 49–58

[10] Zhang W, Wu F, Li J and You Z 2017 Dispersion–precipitation synthesis of highly active nanosized Co$_3$O$_4$ for catalytic oxidation of carbon monoxide and propane *Appl. Surf. Sci.* **411** 136–43

[11] Zhao B, Ke X K, Bao J H, Wang C L, Dong L, Chen Y W and Chen H L 2009 Synthesis of flower-like NiO and effects of morphology on its catalytic properties *J. Phys. Chem. C* **113** 14440–7

[12] Cheng X, Zhu A, Zhang Y, Wang Y, Au C T and Shi C 2009 A combined DRIFTS and MS study on reaction mechanism of NO reduction by CO over NiO/CeO$_2$ catalyst *Appl. Catal. B Environ.* **90** 395–404

[13] Gou Y, Liang X and Chen B 2013 Porous Ni-Co bimetal oxides nanosheets and catalytic properties for CO oxidation *J. Alloys Compd.* **574** 181–7

[14] Yi Y, Zhang P, Qin Z, Yu C, Li W, Qin Q, Li B, Fan M, Liang X and Dong L 2018 Low temperature CO oxidation catalysed by flower-like Ni-CoO: How physicochemical properties influence catalytic activity *RSC Adv.* **8** 7110–22

[15] Wan Ramli W K 2017 Exsolved base metal catalyst systems with anchored nanoparticles for carbon monoxide (CO) and nitric oxides (NO$_x$) oxidation *Newcastle University*

[16] Lew G L, Ibrahim N, Abdullah S, Daud W R W and Ramli W K W 2021 Exsolution enhancement of metal-support CO oxidation perovskite catalyst with parameter modification *IOP Conf. Series: Earth and Environmental Science* **765** 012078

[17] Gou Y, Liang X and Chen B 2013 Porous Ni – Co bimetal oxides nanosheets and catalytic properties for CO oxidation *J. Alloys Compd.* **574** 181–7

[18] Wan Ramli W K, Papaioannou E, Neagu D and Metcalfe I S 2020 Exsolution of nickel alloys anchored nanoparticles on perovskite oxides for CO oxidation *IOP Conf. Series: Materials Science and Engineering* **778** 012059

[19] Argyle M D and Bartholomew C H 2015 Heterogeneous catalyst deactivation and regeneration: A review *Catalysts* **5** 145–269

[20] Popovic J, Lindenthal L, Rameshan R, Ruh T, Nenning A, Löffler S, Opitz A K and Rameshan C 2020 High temperature water gas shift reactivity of novel perovskite catalysts *Catalysts* **10**
[21] Tang C, Kousi K, Neagu D, Portolés J, Papaioannou E I and Metcalfe I S 2019 Towards efficient use of noble metals via exsolution exemplified for CO oxidation Nanoscale 11 16935–44

[22] Soliman N K 2019 Factors affecting CO oxidation reaction over nanosized materials: A review J. Mater. Res. Technol. 8 2395–407

[23] Cheng Y, Qiao M and Zong B 2017 Fischer-Tropsch synthesis Encyclopedia of Sustainable Technologies, ed M A Abraham (Elsevier) pp 403–10