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# Exsolution of nickel alloys anchored nanoparticles on perovskite oxides for CO oxidation

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**Abstract.** Noble metals notably platinum (Pt), is a major element of heterogeneous catalysts, excel in catalysing an extensive number of important catalytic reactions in chemical and automotive industries. Since the increased use of these metals is severely limited because of their high cost and scarcity's, there is therefore an urgent need for the search of alternative transition metal catalysts that are cheaper and more widely available. This can only be practical if the main drawbacks of these transition metals can be impeded for instance the agglomeration of particles under high temperatures operational conditions with their activity enhanced, such that they can directly replace Pt on a weight-to-weight basis. The exsolution of metallic nanoparticles mainly nickel (Ni) at the surface of perovskite oxides in situ has shown remarkable catalytic activity and durability towards carbon monoxide (CO) and nitric oxide (NO) oxidation and in fuel cells. In this study, for CO oxidation reaction, the catalytic capabilities of exsolved Ni nanoparticles can be further enhanced when iron (Fe) and cobalt (Co) are co-exsolved with Ni, as FeNi and CoNi alloy nanoparticles, forming mixed oxide nanoparticles. FeNi alloy nanoparticles exhibit almost ten times site activities as compared to the Ni nanoparticles, owing to the oxide layer formation which then aided the oxidation of CO. Interesting enough, the CoNi alloy nanoparticles exhibit slightly different morphological and chemical transformation due to the difference in oxidation mechanism and the degree of oxidation, which reveal greater site activities towards CO oxidation. These nanoparticles were also subjected to additional compressive strain when they expanded as a result of them being pinned to the support. These results pave the way for new approach in altering the activity of the exsolved materials for various reactions.

## 1. Introduction

Platinum (Pt) is the most versatile metal among the noble metals, and serves as an efficient, multifunctional catalyst for oxidation, hydrogenation and dehydrogenation reactions [1], finding numerous applications in the chemical and petrochemical industries. More than one third of the globally produced Pt is consumed by the primary user of Pt, catalytic converters in the automotive industry alone, where Pt acts as an oxidation and reduction catalyst to control the emission of exhaust gases, namely carbon monoxide (CO), unburned hydrocarbon (HC), and nitric oxides (NO<sub>x</sub>) from petrol and diesel powered vehicles. This is expected, owing to its exceptional catalytic activity and great thermal stability, low reaction affinity with support materials and high resistance towards sulphur. However, the limited supply of Pt leads to high price and its increased demand remains as one of the major obstacles limiting its large-scale applications in current and new technologies, such as fuel cells [2].

For the past decades, researchers have been trying to find cheaper alternatives such as base metals to substitute Pt and attempts have been made to use base-metal catalysts in CO oxidation. Cobalt (Co)



has been found to have good oxidation activity under CO oxidation at low temperatures, although they showed some deactivations at room temperatures, and even more so at high temperatures [3]. Co oxides displayed reversible sulphur poisoning under stoichiometric CO and HC oxidation at higher temperatures (550 °C and above) and the degree of recovery increases with temperatures.

The activities of these base metals are of a similar order of magnitude to those of Pt at relatively low temperature; e.g. at room temperature, but the approaches for catalyst activity comparison tend to be weak, and most studies eluded the direct activity comparison to that of Pt, especially under CO oxidation. Despite being researched extensively, these base metal catalysts are still inferior in terms of rates per metal area or on a weight-to-weight basis, and turnover frequencies (TOFs) under CO and NO oxidation in comparison to Pt. They also have lower stability to sintering and poisoning, and easily react with support materials [4]. The catalytic and stability investigations at high temperatures, and the direct activity comparison to that of Pt are still limited and are not well-described.

The main aim of this paper is to investigate the catalytic activities of exsolved Ni alloy systems that can possibly compete with state-of-the-art commercial Pt powder catalyst in terms of carbon dioxide TOFs under CO oxidation on a weight-to-weight basis. This paper also looks at the oxidation mechanism and the degree of oxidation of these Ni alloys by linking the microstructural changes of the Ni alloy systems to their catalytic behaviours.

## 2. Experimental

### 2.1. Preparation of Catalyst

Ni alloys anchored on perovskite oxide catalysts (powder and pellet forms) were synthesised by a modified solid-state synthesis. High purity precursors including lanthanum oxide ( $\text{La}_2\text{O}_3$ ) from Pi-Kem (> 99.99 %), ceria oxide ( $\text{CeO}_2$ ) from Alfa Aesar (> 99.99 %),  $\text{TiO}_2$  from Alfa Aesar (> 99.6 %), cobalt (III) oxides ( $\text{Co}_3\text{O}_4$ ) from Aldrich (> 99.5 %) and nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) from Acros (> 99%) were used in the appropriate stoichiometric molar ratios, following the balanced perovskites formula. The oxides were dried at different temperatures ( $\text{TiO}_2$  at 300 °C,  $\text{La}_2\text{O}_3$  at 800 °C) and weighed while still warm. The dried powders were then transferred into a beaker and mixed with acetone and ~0.05 wt. % Hypermer KD1 dispersant. An ultrasonic Hielscher UP200S probe was utilised to produce homogenous and stable dispersion of the mixture. The acetone was later evaporated at room temperature under continuous stirring and the content of the beaker was transferred to a crucible and calcined at 1000 °C for 12 hours. The calcined powder was then pressed into pellets (~1.5 g of powder per pellet) and fired in air at 1390 °C for 16 hours to form the perovskite phase in dense pellet form (pore density > 95 %). The as-prepared pellets were further processed via two routes either as pellet or powder. For the preparation of powder, the as-prepared pellets were crushed and ball-milled to produce a powder with a total specific surface area of ~0.5-1.5  $\text{m}^2/\text{g}$  prior to any reduction process. For the preparation of pellet, the as-prepared pellets were first polished on one side (top side) to enable uniform exsolution of metal particles on one side of the pellet only and to prevent the formation of terraces and/or edges surfaces which can suppress the exsolution. Polishing was carried out with a Metaserv 2000 polisher. A MetPrep P1200 polishing paper was used, followed by cloth polishing with MetPrep 6, 3 and 1  $\mu\text{m}$  diamond paste, respectively. The samples were cleaned in between each step with acetone in an ultrasonic bath. Finally, in order to exsolve metal particles on the pellet's surface, the pellets were reduced in a controlled atmosphere furnace, under continuous flow (20  $\text{ml min}^{-1}$ ) of 5 %  $\text{H}_2/\text{Ar}$  at different temperatures with heating and cooling rates of 5 °C/ min, depending on the particle size required and the type of exsolved metals [5].

### 2.2. Catalyst Characterisation

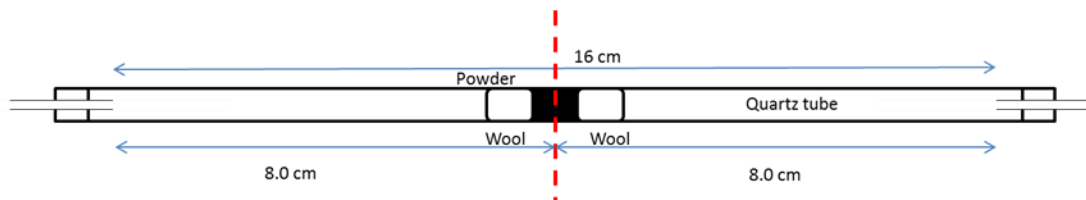
The microstructures of the exsolved Ni alloys were evaluated by Scanning Electron Microscopy (SEM), JEOL JSM-6700F prior to and after catalytic testing. The principle used to map particles and calculated their particle size distribution and population is described in our previous work [6]. The number of particles as well as the diameter of individual particles can be calculated by using ImageJ software. Based on the calculated particle size and population, the exposed area of the particles can be calculated by assuming the particles have hemispheric geometry. The results of this analysis are listed in Table 1.

**Table 1.** Particle characteristics for the exsolved Ni alloy catalysts, including the average particle size, particle population and unit cell parameter, a.

	As prepared (Metallic form)		
	Ni	FeNi	CoNi
Particle size (nm)	30 ± 4	38 ± 5	30 ± 2
Particle population (µm <sup>-2</sup> )	137 ± 10	77 ± 5	144 ± 10
Unit cell parameter, a (nm)	0.41	0.83	0.81
Active sites per unit cell, k	1	2	2

### 2.3. Catalytic Testing

A fixed packed-bed reactor was used for all catalytic tests for powdered catalysts in this work and all catalytic tests were performed at atmospheric pressure. A schematic diagram detailing the assembly of the reactor is shown in Figure 1 below. The flowrate of the feed gases was controlled by electronic mass flow controllers. The gases used were high purity 20% CO/He, 20% O<sub>2</sub>/He and CP grade He (N5, 99.999% minimum purity) provided by BOC Ltd. The total flow rate was maintained at 150 ml/min, measured at the outlet using a Varian digital flow meter (1000 series). An infrared (IR) CO<sub>2</sub> analyser by Emerson (Xstream, Rosemount) was used to analyse the mole fraction of CO<sub>2</sub> at the outlet stream of the catalytic reactor with a minimum measurable limit of 1 ppm of CO<sub>2</sub> (~ 0.027 mmol s<sup>-1</sup> m<sup>-2</sup>).



**Figure 1.** Schematic of the fixed-packed bed reactor for catalytic testing experiment.

The reaction rates in terms of CO<sub>2</sub> production,  $r_{\text{CO}_2}$ , for all Ni alloy systems were calculated as shown in Eq. 1;

$$r^*_{\text{CO}_2} (\text{mol (CO}_2\text{) s}^{-1} \text{ g}^{-1}) = \frac{y_{\text{CO}_2} \times \dot{n}}{w_p} \quad (1)$$

where  $y_{\text{CO}_2}$  is the CO<sub>2</sub> concentrations (in ppm) measured by the IR analyser at the gas outlet,  $\dot{n}$  is the total molar flow rate of the reaction and  $w_p$  represents the weight of the active exsolved Ni alloy powder systems (10 mg). The CO<sub>2</sub> production rates were measured under differential reactor conditions (i.e. isothermal conditions and around 20 % conversion of CO or less) [7].

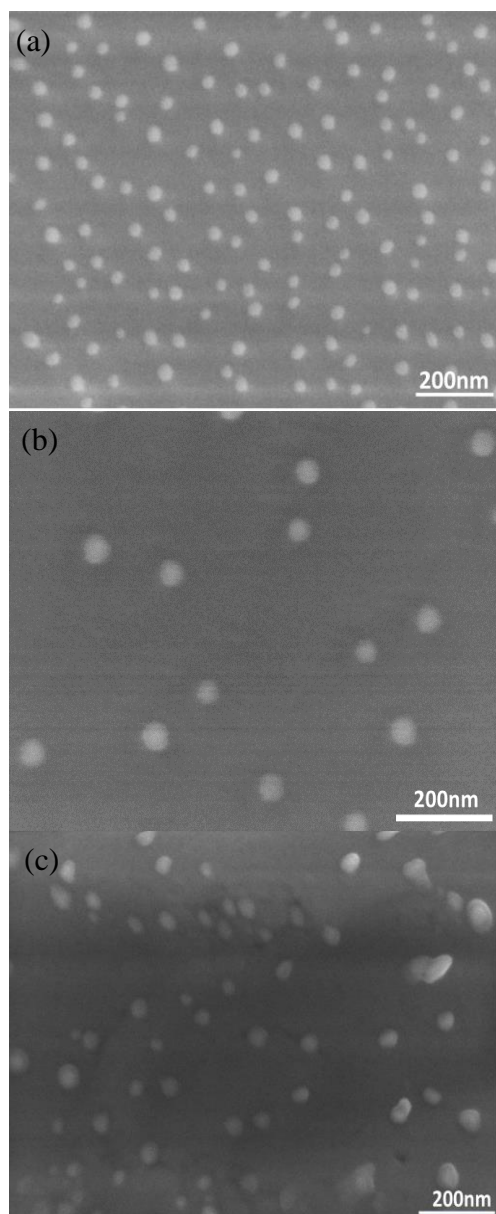
The effect of temperature on  $r_{\text{CO}_2}$  (henceforth, referred as light-off) was investigated by heating up the exsolved systems in an inlet feed streams of 0.6% CO and 1% O<sub>2</sub> from room temperature up to 520 °C, where the temperature was held constant at each temperature step of 20 °C, with a heating rate of 2 °C min<sup>-1</sup> to obtain stable reaction rates measurement, i.e. the rates did not vary more than ± 5 % over 60 min. Another light-off experiment was performed to evaluate the effects of exposure to CO-rich condition on the catalytic activity of these exsolved Ni alloys. The CO-rich condition was introduced by increasing the CO mole fraction,  $y_{\text{CO}}$  (0.5-18.8%) while keeping the O<sub>2</sub> mole fraction,  $y_{\text{O}_2}$  constant at 0.64% at 520 °C.

## 3. Results and Discussion

### 3.1. Catalyst Microstructure

**Figure 2** shows the SEM micrographs of the fresh powdered catalyst systems: (a) Ni, (b) FeNi and (c) CoNi powder systems. The powder systems revealed to have rounded exsolved metal particles, and the

exsolved metal particles were uniformly distributed across the surface of the powder systems, which is consistent with the materials produced by the exsolution method. However, the limited control of the particles population in powder form resulted in fewer FeNi particles were exsolved for FeNi system because of the possible existence of different types of native surfaces such as kinks or edges, which can suppress the exsolution. These surfaces are not easily polished or cleaved in powder sample which makes it more difficult to control the extent of the exsolution [6]. Therefore, in order to observe the changes in particle characteristics prior to and following catalytic testing, model pellet systems were used.

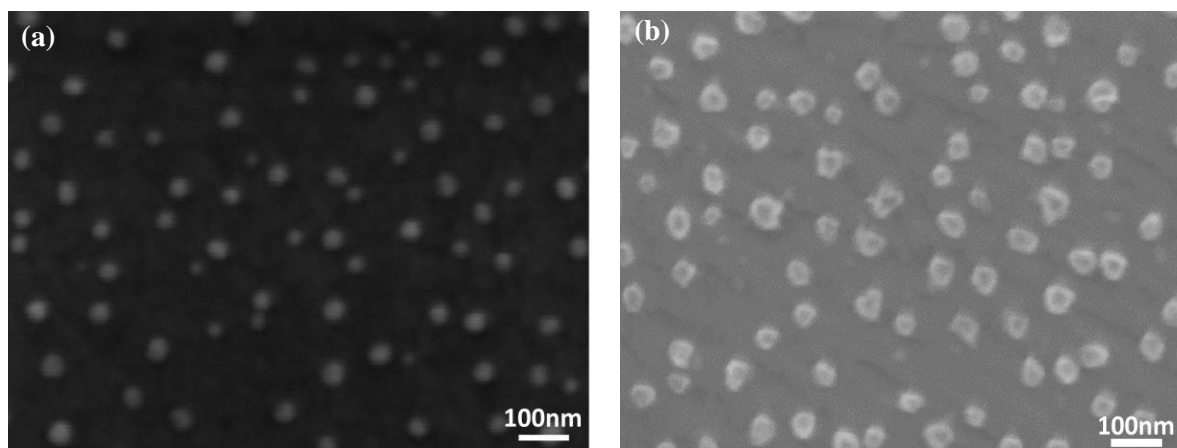


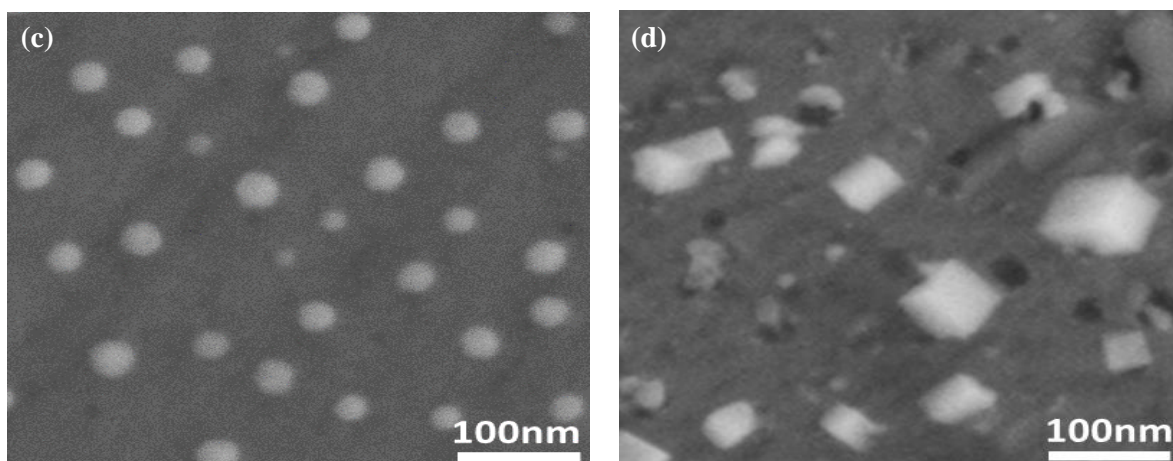
**Figure 2** SEM micrographs of the as-prepared (metallic state) exsolved Ni alloys powders: (a) Ni, (b) FeNi and (c) CoNi

The surface microstructures of these catalysts systems (model catalyst) prior to and following experiments were scanned under SEM using the model pellet systems. Since both FeNi and Ni pellet systems display similar faceted and enlarged particles after subjected to catalytic experiments, only the surface morphologies of the Ni pellet system were shown to avoid redundancy. **Figure 3** compares the surface morphologies of the (a, c) fresh and (b, d) post-experimental pellet surfaces of Ni and CoNi pellet systems. The particle size analyses revealed that the size of the exsolved Ni and FeNi nanoparticles expanded following catalytic experiments, from an initial average particle size of 30 and 38 nm (refer **Table 1**) to around 39 and 54 nm, respectively.

For the exsolved Ni system, the increased size of Ni particles exhibited slightly larger values of oxidised-to-fresh size ratio than the expected lattice expansion from metallic Ni ( $\text{Ni}^\circ$ ) to rock salt nickel (II) oxides ( $\text{NiO}$ ), while still retaining the metal core due to the slower  $\text{O}_2$  inward diffusion of Ni. For exsolved FeNi system, the particle size ratio between the fresh and oxidised surfaces was found to be around 1.42. This value is in agreement with the reported lattice expansion from metallic Fe (lattice parameter,  $a = 0.285 \text{ nm}$ ) or FeNi ( $a > 0.357 \text{ nm}$ ) to mixed Fe oxides ( $a > 0.835 \text{ nm}$ ), associating to oxides to metallic particle size ratio of  $\sim 2.93$  [8]. This finding also supports the works of other studies that link the surface oxidation of the particles to the increase of the L3/L2 ratio of Fe upon oxidation, although the value was smaller than the oxidation of Fe as it is believed to be the effect of alloying Ni to Fe [9,10]. By comparing the particles population between the fresh surface (67 particles  $\mu\text{m}^{-2}$ ) and the oxidised surface (75 particles  $\mu\text{m}^{-2}$ ), no significance changes were observed, which confirms the stability of these pinned Ni and FeNi particles upon subjected to oxidising and CO-rich conditions, which is ascribed to their strong metal-support interaction as proven in previous work by Naegu et al. (2017).

However, a different oxidation mechanism was observed for CoNi pellet system which involved a phase transformation from metallic Co into the predominant  $\text{Co}_3\text{O}_4$  spinel structures with an oxide intermediate phase of the rocksalt CoO structure, following a rather complicated diffusion mechanism known as the Kirkendall Effect. The appearance of cube-like structures and distinct dark spots near to the particles, believed to be empty sockets, were observed, which were not observed on the Ni and FeNi surfaces. Restructuring of CoNi particles were observed after performing the catalytic testing following the arrangement of such: Light-off, CO-rich condition, Light-off. It was believed that during the first light-off, the formation of hollow cores occurred. This was caused by a much faster Co outward diffusion compared to the inward  $\text{O}_2$  diffusion once cobalt (II) oxide (CoO) is formed. This then resulted in the hollowing of the metal cores, expanding the particles laterally. The metal particles were also subjected to additional compressive strain when they expanded during light-off as a result of them being pinned to the support to begin with. Although the lattice expansion from metal to oxide phases was considerably larger than the metal-support expansion experienced by the support lattice, due to the lower  $\text{O}_2$  diffusion rates, these strain-induced sites which are normally present at the metal oxide-support interface have been associated to provoke changes on the catalytic activities of supported metal catalysts [12]. It has been reported that this can affect the catalytic activities of metal catalysts, due to the modified electronic structure at the metal-support interface which then causes a perturbation in the shape formed by the expanding metal particles [13]. The dominant effect of hollowing causes the particles to dislodge from their sockets. Several particles were restructured into cubic structures and they also appear to relocate at the edge of their sockets, and at an angle, revealing a specific active geometric plane [11]. These empty sockets, however, effectively reduce the population of the active structures to almost half of the initial particle population, equating to around 44 cubes  $\mu\text{m}^{-2}$ , from an initial population of 144 particles  $\mu\text{m}^{-2}$ .





**Figure 3** SEM micrographs of the as-prepared (metallic state) exsolved Ni alloys in pellet forms following the same testing procedure as the powder form: (a) FeNi (Metallic), (b) FeNi (Oxidised), (c) CoNi (Metallic) and (d) CoNi (Oxidised).

### 3.2. Catalytic Activity/ Turnover Frequencies (TOF)

**Figure 4** shows the CO<sub>2</sub> production rate for the CO oxidation reaction, as a function of temperature for all three powder systems; Ni, FeNi and CoNi. However, it should be noted that, as revealed by the SEM images (See **Figure 2**), the FeNi system exhibits lower particle population as compared to Ni and CoNi. In order to better compare the site activities of all systems with each other and to the literature, their respective turnover frequencies (TOFs) were calculated. The active sites were assumed to be associated with the metal oxide particles and that each surface metal atom provides one active site. The TOFs, defined as the number of CO<sub>2</sub> molecules produced per active site per second are given by Eq. 2.

$$TOF(s^{-1}) = (N_A \times r_{CO_2} \times a^2) / (A_{ps} \times A_p \times k) \quad (2)$$

where  $N_A$  is the Avogadro number (mol<sup>-1</sup>),  $r_{CO_2}$  is the rate of CO<sub>2</sub> production,  $A$  is the catalyst area with exsolved nanoparticles in oxidised form,  $A_e$  is the exposed metal area per catalyst area,  $a$  is the crystal lattice unit cell parameter of the particles and  $k$  is the average number of metal sites per unit cell face (see **Table 1**). For the NiO rock-salt structure,  $k = 1$ , for mixed (FeNi)<sub>3</sub>O<sub>4</sub> and the (CoNi)<sub>3</sub>O<sub>4</sub> spinel structure,  $k = 2$  [14].

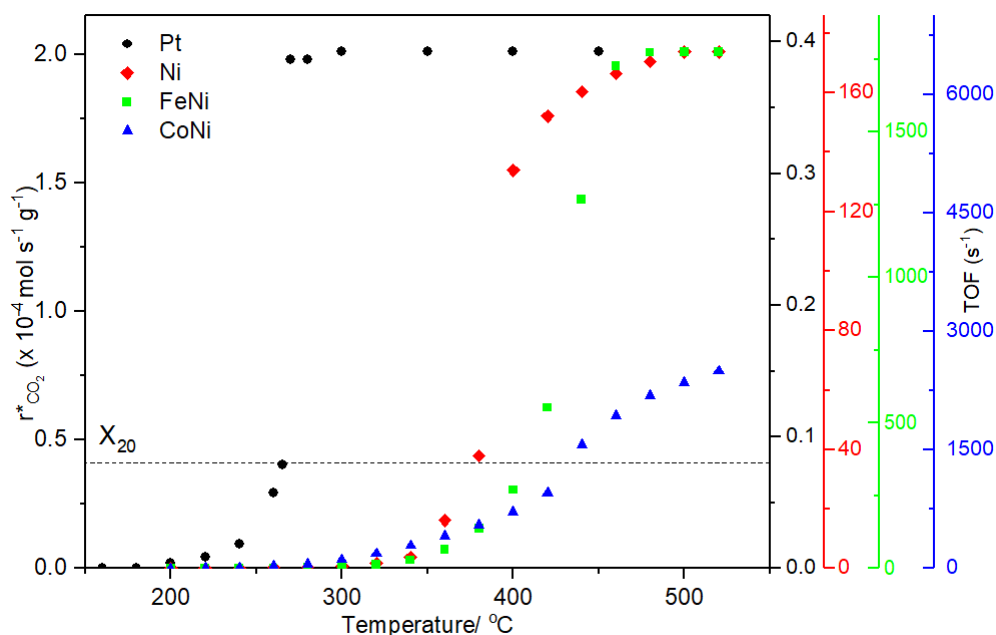
The corresponding TOF values were plotted against temperature on the right y-axis in Figure 4 for all catalysts. Consistent with a previous report [11], the TOF values for all exsolved catalysts are of the order of several hundreds of s<sup>-1</sup>.

Interestingly though, under the same conditions, the TOF values for FeNi are roughly 10 times higher as compared to Ni system. This difference largely originates in the fact that the particle population of the FeNi sample is roughly half of that in the Ni system. These results indicate that the activity of Ni-based exsolved nanoparticles for the CO oxidation reaction can be further enhanced by alloying with other earth-abundant metals such as Fe. Ni system recorded TOF around 35 s<sup>-1</sup> at 380 °C while FeNi system exhibited TOF values of up to 350 s<sup>-1</sup> at 400 °C (~20% of CO conversion.). The light-off following exposure to CO-rich condition follows similar rate trend as the first ones for both Ni and FeNi systems, confirming the stability of these exsolved materials yet again upon exposure to harsh condition. The NiO and Fe oxides structures formed during the first light off, as discussed previously aided the total oxidation of CO, as it is evident from the high TOFs reported under light-off, owing to the strong CO removal activity by acting as a promoter to remove CO by weakening the C-O bond for easier dissociation to CO<sub>2</sub> [15].

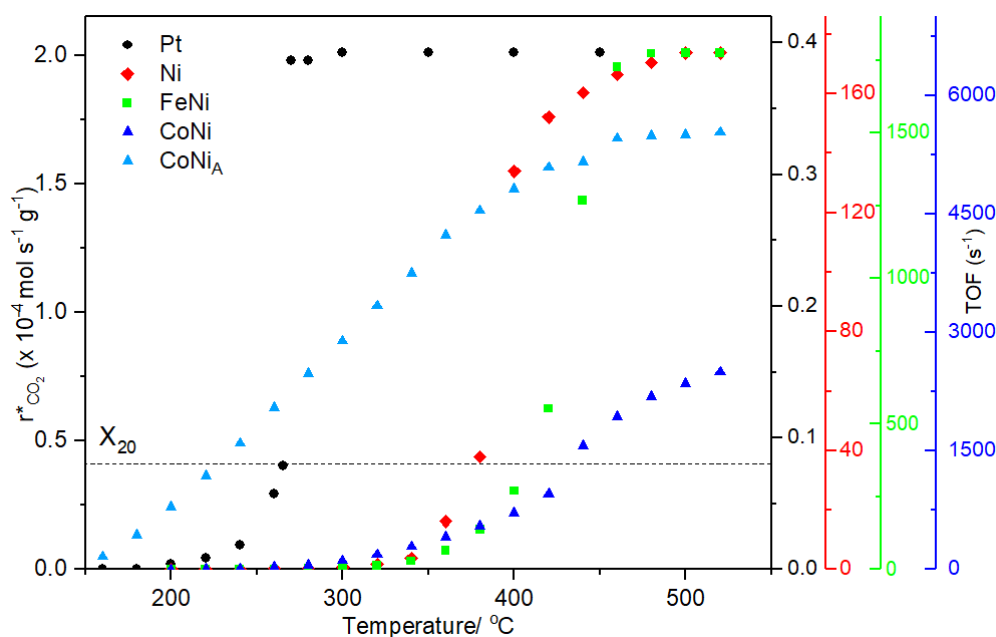
At 420 °C, CoNi exhibited TOF of almost 1000 s<sup>-1</sup>. These values are a few orders of magnitude higher than TOF recorded for Pt (~0.07 s<sup>-1</sup> at 265 °C) and values reported in literature for base metal and metal oxide nanoparticles [16]. Unlike Ni and FeNi systems, higher TOF values were recorded in the second light-off, as if the CoNi particles were activated upon exposure to oxidised and CO-rich condition. CoNi<sub>A</sub> demonstrated TOF of ~1000 s<sup>-1</sup> at a much lower temperature of 200 °C.

Surprisingly, these enhanced TOF values were achieved by an essentially less active area, as it is evident from the particle populations given in Figure 4(d). This corroborates most studies that confirm that the activities of Co-based catalysts are known to be strongly dependent upon the microstructure, including the particle shapes, sizes and exposed planes, manipulating the Co microstructure through pre-treatment in order to form specific active structures to suit specific reactions such as CO oxidation. As highlighted in Figure 5(b), CO oxidation favours the CoNi system at lower temperatures while at higher temperatures, the CO<sub>2</sub> production favours that of Pt.

(a)



(b)



**Figure 4** CO<sub>2</sub> production rates and TOF (s<sup>-1</sup>) for exsolved Ni, FeNi and CoNi powders in CO oxidation, as a function of temperature for (a) fresh and (b) after exposing to CO-rich condition at 520 °C, using the indicated powder catalysts. Inlet flowrate of 450 ml min<sup>-1</sup> with a feed gas mixture of 0.6% CO and 1.0% O<sub>2</sub>. The right y-axis shows the corresponding CO conversion values calculated.

#### 4. Conclusions

In this work, a novel approach for tailoring the catalytic activities of Ni alloy catalyst systems by inducing high, long-lasting activity, to rival Pt for CO oxidation on a weight-to-weight basis by having pinned nanoparticles on the perovskite support. The activities of these exsolved Ni alloy systems, expressed in TOFs, are shown to be comparable to that of Pt catalysts reported in the literature, by having TOFs in the range of  $1000 \text{ s}^{-1}$ . This study also shows that the pinned characteristics of these exsolved metal pellet systems aid the stability of the systems, inhibiting the agglomeration of particles at high temperatures, especially for Ni and FeNi systems. Unlike Ni and FeNi, CoNi particles were seen to restructure into semi-planted nanocubes, probably revealing active geometric planes with the presence of Co ions, following an oxidation mechanism known as the Kirkendall effect. The enhanced TOF values were observed for exsolved CoNi system upon exposure to CO-rich environment, insinuating the fact that CO acts as structure promoter for CoNi particles. Further substitution of Co in the exsolved Ni system demonstrated relatively high activities in comparison to those reported in the literature, especially in the low-temperature region, and these findings highlight the role of particle confinement in producing enhanced TOFs during reactions. Not

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