

# A new hollow fibre catalytic converter design for sustainable automotive emissions control

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**Abstract**

State-of-the-art catalytic converters need an ever-high amount of precious-metal catalysts to meet stringent emission regulations. This research reveals an alternative design based on micro-structured ceramic hollow fibre substrates, yielding high conversion of pollutants at low catalyst costs, as well as a unique benefit of low pressure-drop, leading to high engine performances.

**Keywords:** Catalytic converter, Palladium, CO oxidation, ceramic hollow fibre, Geometric Surface Area.

## 1. Introduction

There is an enormous number of vehicles in the world powered by fossil fuels. For the UK only, around 99% of 31 million cars licensed by 2017 are fuelled by petrol or diesel (Statistical Release of Department for Transport, April 2018, GOV.UK), with 3.1 million new vehicles registered in 2017 of a similar case, despite the quick growth of alternatives to fossil fuels [1]. Currently, each vehicle on roads needs at least one catalytic converter in the emissions control system converting toxic gases (CO, NO<sub>x</sub>, and hydrocarbons) into harmless emissions such as N<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>. As the key component within an emissions control system, a catalytic converter normally consists of a structured substrate (cordierite or metal-based monolith) with high geometric surface areas (GSA), in order to minimise the amount of expensive precious metal catalyst wash-coated onto it [2,3]. Other important design requirements for such structured substrates include low-pressure drops in order for good engine performance, e.g. less fuel consumption and as thus reduced CO<sub>2</sub> emissions, and small volumes to enhance vehicle design flexibility etc.[4]. Generally, a monolithic substrate with a higher GSA has a larger number of smaller parallel channels and as thus higher values of cells per square inch (CPSI), as shown in Figure 1. This enables the formation of thinner catalytic wash-coating layers, and consequently lower diffusion resistance within the catalyst layer and higher conversion efficiency, by using possibly a less amount of precious-metal catalysts. Unfortunately, this can be at the expense of decreased engine performance due to the increased pressure drops of catalytic converters. As shown in Figure 1, increase of CPSI results in higher GSA at a given volume, while a sharp increase in pressure drop. As a result, conventional monolith substrates of 400 and 600 CPSI have been widely employed in automotive industry, even though higher CPSI values such as 900 can be manufactured.

Cordierite or metal-based monolith substrates have served as the cornerstone of state-of-the-art catalytic converters for over 40 years. With the more stringent emissions standards put into

force, i.e. the dramatically tightened Euro-6 in 2014-2015, the design limitation of conventional substrates aforementioned is turning into a serious concern. To meet the required emission standards, more precious-metal catalysts have to be used, substantially increasing the costs of emissions control [5,6]. As a result, the emissions control system is becoming the single most costly bought-in component of a large commercial vehicle, even approaching the costs of the engine itself [7].

To address such challenges, e.g., abating toxic emissions efficiently by using an as low as possible amount of precious-metal catalysts, and maintaining good engine performance at the same time, breakthroughs in catalytic converter designs are needed. In one of our previous researches [7], it was found that “impregnating” a small amount of Pd (without wash-coating) into a more porous ceramic hollow fibre substrate, which can be bundled together to form a mechanically and thermally robust monolithic configuration, led to a very efficient conversion of CO to CO<sub>2</sub>. Based on this, we here reveal a further step change in catalytic converter design by addressing controlled incorporations of catalytic wash-coating materials into the oriented radial micro-channels of a ceramic hollow fibre substrate. CO oxidation and pure Pd supported on gamma-alumina were employed at example reaction and catalyst, respectively. As shown in Figure 1, the hollow fibre substrate with radial micro-channels provides GSA approaching to 900 CPSI, but still maintains a low pressure drop. In addition to the high conversion efficiency due to the low diffusional resistance inside catalytic layers, the incorporation of washcoating further lowers light-off temperatures without compromising pressure drops, by maintaining channel dimensions comparable to or even larger than monolithic counterparts of 400 CPSI.

## **2. Experimental**

### **2.1 Materials**

$\alpha$ -alumina ( $\text{Al}_2\text{O}_3$ ) powder (1  $\mu\text{m}$ , 99.9 % metal basis, surface area 6-8  $\text{m}^2 \text{g}^{-1}$ , Inframat Corporation) was used as supplied. N-Methyl-2-pyrrolidone (NMP, synthesis grade, Merck) and Arlacel P135 (Polyethyleneglycol 30-dipolyhydroxystearate, Uniqema) were used as the solvent and dispersant respectively. Poly(methyl methacrylate) (PMMA) (Radel A-300, Ameco Performance, Greenville, SC) was used as the polymer binder. A mixture of NMP/ethanol (HPLC grade, VWR), and distilled water were used as the internal and external coagulants, respectively.

$\gamma$ -Alumina ( $\text{Al}_2\text{O}_3$ ) powder (99.995%, surface area  $100 \pm 30 \text{ m}^2 \text{g}^{-1}$ , Inframat Advanced Materials) was used for the wash-coating layer without further purification. Hydrochloric acid (HCl) and palladium(II) chloride ( $\text{PdCl}_2$ ) (99.9% metal basis, min 59.0% Pd, Alfa Aesar) were used to prepare a metal salt precursor solution.

### **2.2 Fabrication of ceramic hollow fibre catalytic converters**

Micro-structured ceramic hollow fibre substrates were first prepared via a phase-inversion assisted process [8]. Controlled amounts of Gamma- $\text{Al}_2\text{O}_3$  (between 0 and 10 wt.%) as the exemplified wash-coating material were then incorporated into these substrates (W-0, W-3, W-5, W-8 and W-10 in Table 1), before the introduction of approximately less than 0.7 wt.% of Pd for all the samples by wet impregnation, forming the hollow fibre catalytic converter after reduction for CO oxidation. Further details of this process can be found in the supplementary document.

### **2.3 Performance evaluation – CO oxidation**

The reaction was performed under an atmospheric pressure (Figure S2). Prior to the test, the hollow fibre catalytic converter was reduced at 450  $^\circ\text{C}$  for 1 hour, using a mixture of 5  $\text{ml min}^{-1}$   $\text{H}_2$  and 30  $\text{ml min}^{-1}$  Argon. A hollow fibre catalytic converter sample of

50 mm long was mounted within a cylindrical quartz tube, with the GHSV of  $\sim 43,250$   $\text{h}^{-1}$ . Mass flow controllers (Model 0154, Brooks Instrument) were used to maintain a total gas flow rate at  $100 \text{ ml min}^{-1}$ . A reactant gaseous mixture of  $50 \text{ ml min}^{-1}$  air and  $50 \text{ ml min}^{-1}$  (10% CO in 90% Argon) was fed into the reactor system, representing the lean-burn conditions. The gas mixtures flow was pre-heated to the reaction temperature and placed in an upstream motion through the hollow fibre catalytic converter. An on-line gas chromatograph (Varian 3900) equipped with a thermal conductivity detector was connected to the reactor outlet via gas sampling tubing. In addition, a bubble flow meter was used to measure outlet flow rate. Sampling for analysis was recorded every 30 minutes after stabilisation of each temperature intervals. A series of light-off temperature performance tests were carried out until 100% conversion was achieved.

### **3. Results and Discussion**

#### **3.1 Micro-structures of hollow fibre substrate**

Different from the existing cordierite or metal-based monoliths, micro-structured alumina hollow fibres (Figure 2) offer unique radial micro-channel inside the fibre wall, significantly enlarging GSA to approximately  $40 \text{ cm}^2 \text{ cm}^{-3}$ . This is comparable with the GSA of the commercial monolith of 750 CPSI (Table 2), while with the hydraulic channel diameter almost doubled, indicating pressure drops much lower than the commercial counterpart. Moreover, the inner diameter of hollow fibre substrate was measured at approximately 1.6 mm (Figure 2), which is approximately 60% and 170% larger than the channels of a 400 and 900 CPSI monoliths, respectively[7]. The correlation between pressure drops and hydraulic diameter has been well studied and can be calculated by Darcy-Weisbach Equation which was further proved by various studies on this subject[1]. Low pressure drops enable faster auto-ignition, due to the

high intake pressure which reduces the premixing time before combustion happens in engines, and increases burning efficiency that reduces the unburned exhaust [9]. This means, by using the hollow fibre substrate, low pressure drops enabling good engine performance and the high GSA values can be achieved at the same time, which is so far challenging for state-of-the-art catalytic converter substrates commercially available. It is also worth to note that, an even higher value of GSA can be achieved by controlling the substrate fabrication parameters [7].

The outstanding GSA values obtained would enable the formation of thinner catalytic wash-coating layers with lower diffusion resistance and reduce the amount of precious-metal catalyst needed. Unfortunately, there are so far very limited investigations incorporating catalytic wash-coatings inside such oriented micro-channels, mainly due to the fact that the advantages of using hollow fibre substrates for emissions control are not yet well disseminated. As well as the challenge that the diameters of these micro-channels are of only several tens of micrometres (Figure 2), which is almost same as the thickness of catalytic wash-coating employed in existing monolith substrates, thus requiring new ideas and methodologies for incorporating wash-coating materials.

### **3.2 Distribution of the catalyst inside hollow fibre substrates**

The introduction of gamma- $\text{Al}_2\text{O}_3$  increases the specific surface area of the substrate samples effectively [10], between around 3 and 7 times when the loading of gamma- $\text{Al}_2\text{O}_3$  was increased from 3wt.% to 10 wt.% (Table S5). Meanwhile, morphologies of gamma- $\text{Al}_2\text{O}_3$  inside the oriented micro-channels turn from wash-coating layers (W-3 & W-5 in Figure 3) into micro-packings (W-8 & W-10 in Figure 3), indicating potentially increased transport resistance when over-loaded with the wash-coating material (Figure S3). Similar trends were also observed at the inner surface of the hollow

fibre substrate (Figure S4), with a very thin and porous gamma-Al<sub>2</sub>O<sub>3</sub> skin-layer, which “covers” the opening ends of micro-channels, formed at 5 wt.% of loading. With further increased loadings of gamma-Al<sub>2</sub>O<sub>3</sub>, this skin-layer becomes thicker, leading to higher BET surface areas but more transport resistance at the same time.

Pd as the catalytic phase was found uniformly dispersed inside the wash-coated hollow fibre substrates, with the particle size of around 10 nm (Figure 4). The darker shades on the surface (Figure 4) were caused by the height differences of the sample during analysis, instead of agglomeration, which is in line with the EDX analysis. EDX analysis confirms the presence of Al, O, and Pd, with the intensities of the corresponding peaks of very similar ratios at different locations (Figure S5). Moreover, by incorporating an increasing amount of gamma-Al<sub>2</sub>O<sub>3</sub>, with the very similar loading of Pd, the inner surface of hollow fibre catalytic converter looks darker (Figure S6), which can be linked to the presence of more gamma-Al<sub>2</sub>O<sub>3</sub> and thus deposition of metal catalyst on the inner surface (Figure S4).

### **3.3 Catalytic performance for CO oxidation**

The resultant hollow fibre catalytic converters show excellent performance for CO oxidation (Figure 5). For W-3, W-5, W-8, and W-10, the one with various quantities of wash-coating materials, complete conversions of CO were achieved at temperatures below 200 °C, which was around 30 °C lower than the one without gamma-Al<sub>2</sub>O<sub>3</sub> (W-0). This demonstrates the effectiveness of incorporating suitable wash-coating materials inside the oriented micro-channels of hollow fibre substrates (Figure 5), considering the very similar loading of precious-metals for all the samples involved in this study (Table 1).

By comparing the light-off temperature of T50, the temperature when 50% of CO was converted into CO<sub>2</sub> (Table 1), W-3 is almost 30 °C lower than W-0, mainly due to the



presence of around 12 mg of  $\gamma\text{-Al}_2\text{O}_3$  inside the oriented micro-channels (Figure 3, Figure S4), considering the same amount of Pd incorporated. The similar trend applies for the further decreased T50 from W-3 to W-5, despite the formation of a porous skin-layer on the inner surface of W-5, together with a slightly thicker wash-coat layer inside the micro-channels (Figure 3, Figure S4). This also indicates that a thin and porous wash-coat layer on the inner surface will not impair the efficiency of hollow fibre catalytic converter. The further increment of wash-coating materials leads to increasing T50 from 187 °C of W-5 to 193 °C of both W-8 and W-10, despite larger BET areas (Table S5). This can be linked to the thicker wash-coating layers on the inner surface of W-8 and W-10, as well as more densely packed  $\gamma\text{-Al}_2\text{O}_3$  inside their micro-channels (Figure 3, Figure S4). This increases the diffusional resistance of the catalytic wash-coating, resulting in less effective interactions between emissions and precious-metal catalyst, a typical case when thicker catalytic wash-coating layers are employed in monolithic catalytic converters[11]. Furthermore, the active catalytic phase of W-8 and W10 is more concentrated in the wash-coating layer on the inner surface, instead of inside the micro-channels like W-5, a second reason for the higher T50. Such a segregation of catalytic active phase offers less effective surface to be in direct contact with reactants, thus reducing the number of sites taking place in reactions. This further addresses the importance of incorporating catalytic wash-coatings into the micro-channels for promoting converting performance of this catalytic converter design.

In contrast to our previous study [7] (Table 1), no wash-coating materials were used for neither W-0 nor MT3. W-0 has a much higher amount of Pd, while its T50 is nearly 25 °C higher. This is mainly due to the different reaction conditions, such as 10 times of CO concentrations involved in this study and less micro-channels. While under the similar testing conditions, W-3 to W-10 perform better than MT3 in terms of lower T50.

For instance, T50 of W-5 is approximately 20 °C lower. Combining with the difference between W-0 and MT3, it is clear that a suitable quantity and morphology of wash-coating layer inside the oriented micro-channels of hollow fibre substrate is critical for good emissions control performance.

By further comparing with M400, a commercially available sample, W-5 offers the same T50 as M400 under the conditions of 10 times of CO concentration, despite around the twice amount of PGM loading, yielding approximately 5 times of Turnover Frequency (TOF) if all the catalytic active phase participates in the reaction, another indicator of greater interactions between Pd and CO, when catalysts are incorporated inside the micro-channels. This enables further improvement of hollow fibre catalytic converter by forming more uniform wash-coating layers inside the oriented micro-channels. Moreover, broader testing conditions, such as higher operating temperatures, testing gases containing HCs, NO<sub>x</sub> and H<sub>2</sub>O etc., as well as longer testing time etc. should be considered in order for a more comprehensive comparison with commercial counterparts.

#### **4. Conclusions**

We here reported the development of a new and efficient catalytic converter design, by incorporating exemplified wash-coating materials into micro-structured ceramic hollow fibre substrate followed by impregnating Pd as the active phase. With less than 0.7 wt.% of catalyst, the reported new design lowers the light-off temperatures to the same level of existing commercial counterparts, at lower pressure drops and greater catalyst efficiency, by eliminating the design limitations of current monolithic counterparts. This could motivate further development of more advanced catalytic converter at lower costs, with greater engine

performance saving fuels and reducing CO<sub>2</sub> emissions, and of smaller volumes benefiting design flexibility of cars.

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## **Highlights**

- New micro-structured ceramic hollow fibre substrate for automotive emissions control.
- High geometric surface areas and low pressure drop can be achieved at the same time.
- Catalytic wash-coating inside the radial micro-channels of several tens of micrometres.
- Efficiently converting CO at light-off temperatures comparable to commercial monolithic substrate.

## Tables

**Table 1.** Comparison of CO oxidation performance

Sample	PGM loading (g/ft <sup>3</sup> )	Gamma-Al <sub>2</sub> O <sub>3</sub> (mg)	Space velocity (h <sup>-1</sup> )	CO (%)	O <sub>2</sub> (%)	Inert gas (%)	Light-off temperature (T50, °C)	Reference
M400*	75 (Pt)	-	50,000	0.5	1	98.5	187	[7]
MT3**	16 (Pd)	0	50,000	0.5	1	98.5	201	
W-0	164 (Pd)	0	43,250	5	10	85	224	This study
W-3	168 (Pd)	12	43,250	5	10	85	195	
W-5	184 (Pd)	20	43,250	5	10	85	187	
W-8	180 (Pd)	31	43,250	5	10	85	193	
W-10	184 (Pd)	40	43,250	5	10	85	193	

Each sample of W-0 to W-10 is of approximately 130 mm in length

\* 400 CPSI commercial cordierite monolith substrates, coated with a 0.96 wt% Pt/CeO<sub>2</sub> wash-coat

\*\* Hollow fibre substrates without wash-coating materials

**Table 2.** Comparison of GSA values between monolithic converter and hollow fibre converter

Conventional monolith (CPSI)	Geometric Surface Area (GSA) $\text{cm}^2 \text{cm}^{-3}$	Reference
400	29.3	
600	36.2	
750	40.2	[12]
900	43.7	
Ceramic hollow fibre	40.7	This study

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**Figure 4.** TEM images of Pd dispersed throughout the wash-coated hollow fibre substrates

**Figure 5.** CO Oxidation light-off curves for samples at different wash-coat loadings of 0, 3, 5, 8 and 10 wt.%.



Figures

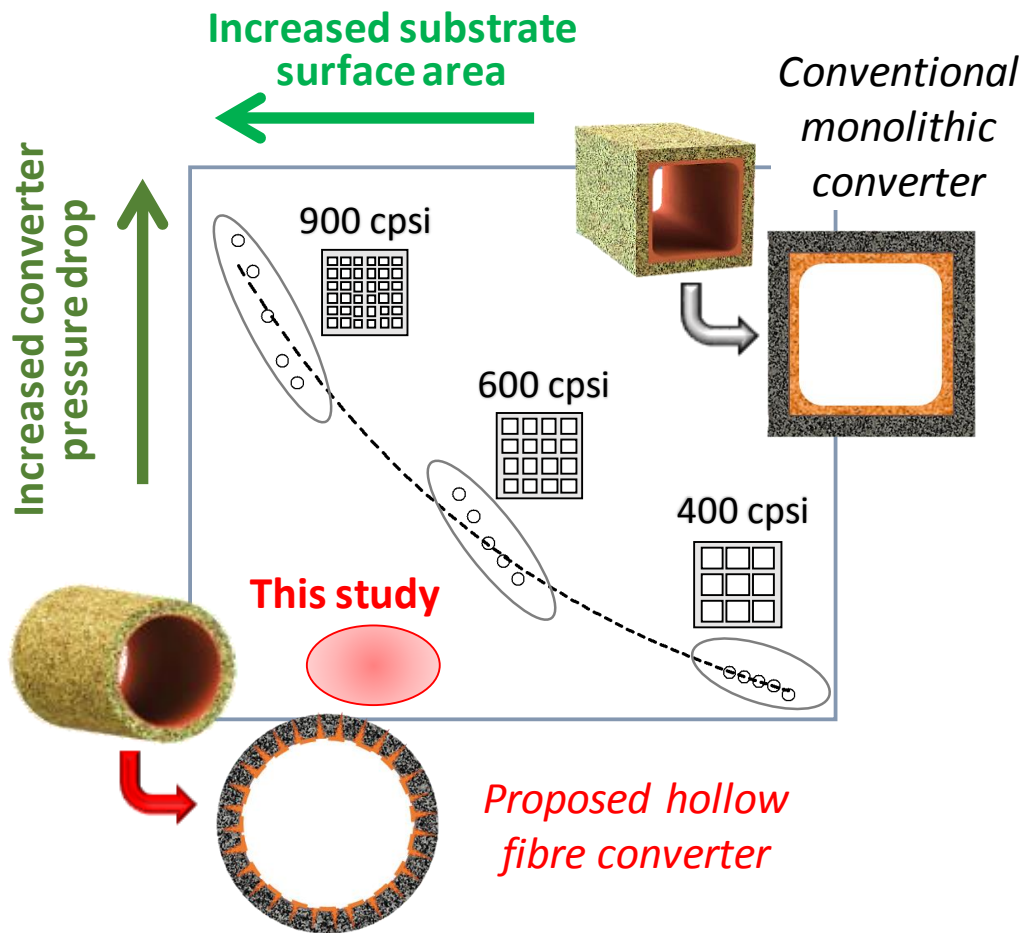


Figure 1

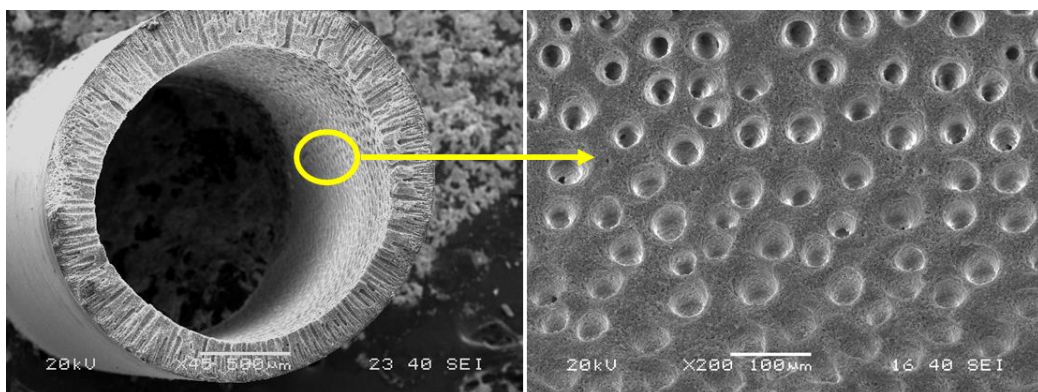


Figure 2

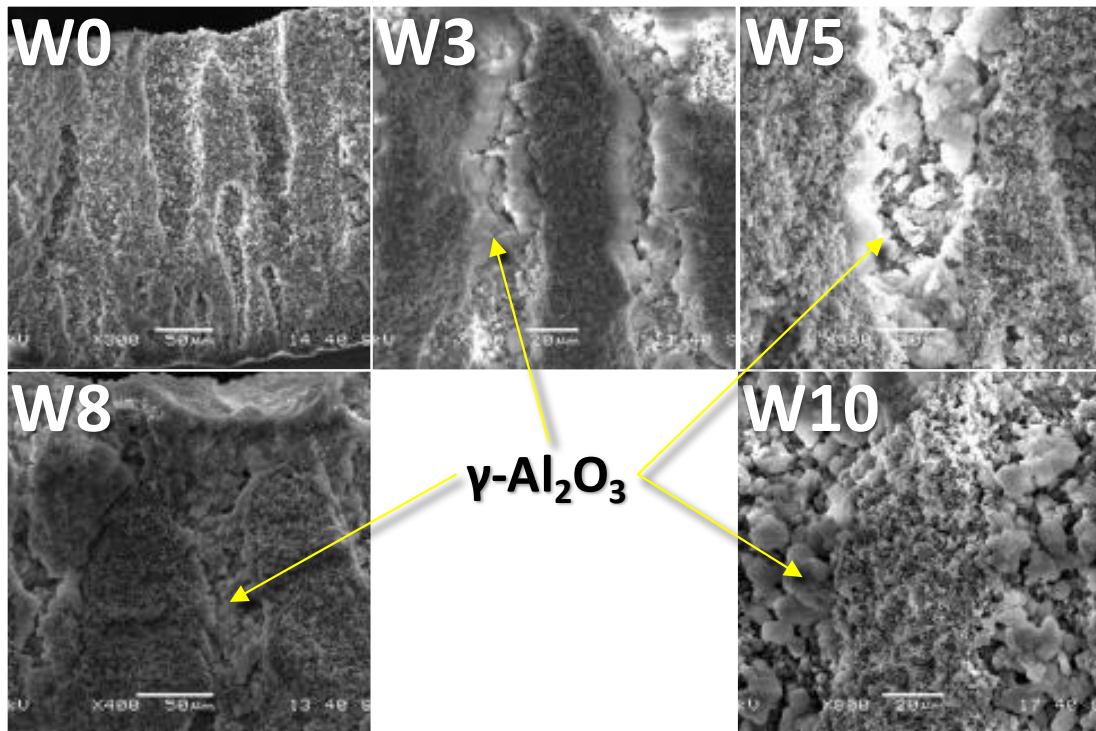


Figure 3

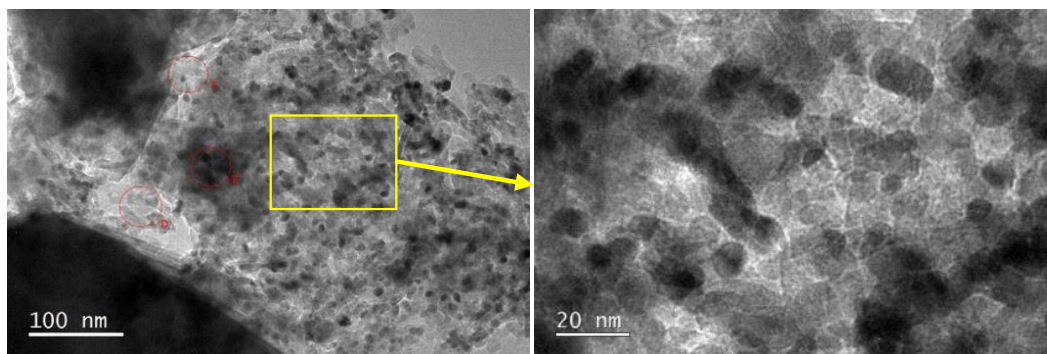
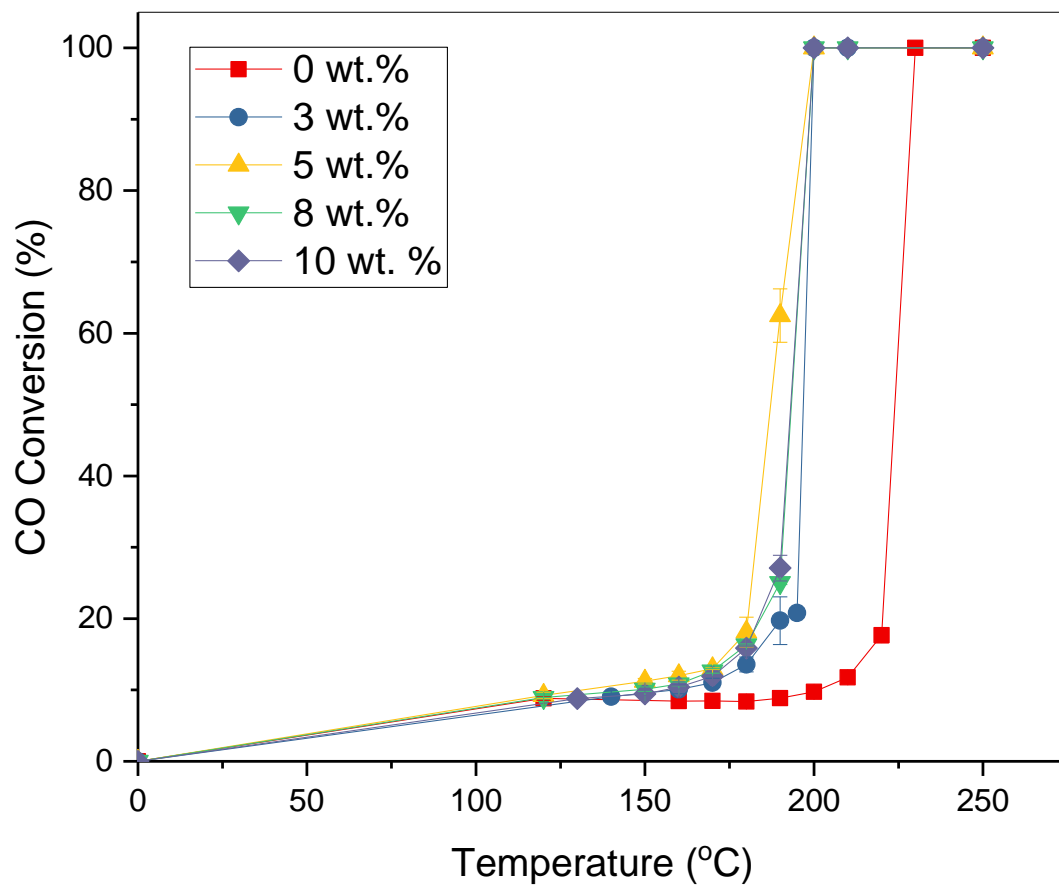


Figure 4



**Figure 5**