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### Citation for published version:

Benavente, P, Cardenas-Lizana, F & Keane, MA 2017, 'Selective Production of Carvacrol from Carvone over Supported Pd Catalysts', *Catalysis Communications*, vol. 96, pp. 37–40.  
<https://doi.org/10.1016/j.catcom.2017.03.026>

### Digital Object Identifier (DOI):

[10.1016/j.catcom.2017.03.026](https://doi.org/10.1016/j.catcom.2017.03.026)

### Link:

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### Document Version:

Peer reviewed version

### Published In:

Catalysis Communications

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**Selective Production of  
Carvacrol from Carvone  
over Supported Pd Catalysts**

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## **Abstract**

The selective conversion of biomass-derived carvone in H<sub>2</sub> was studied over (Al<sub>2</sub>O<sub>3</sub>, C and CeO<sub>2</sub>) supported Pd (mean size 2.8-3.0 nm), taking bulk Pd as benchmark. 100% carvacrol yield was achieved over Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/C and bulk Pd at an inlet H<sub>2</sub>/Carvone = 1/6, with appreciably higher rates for the supported catalysts. Carveol formation over Pd/CeO<sub>2</sub> was attributed to -C=O activation at surface oxygen vacancies (confirmed by O<sub>2</sub> titration) generated during TPR. Carvotanacetone and carvomenthone formation were observed at H<sub>2</sub>/Carvone > 1/6.

**Keywords:** Carvone; carvacrol; hydrogenation; supported Pd.

## 1 Introduction

Carvone is a terpenoid obtained at low cost by steam distillation of spearmint oil or nitrosochlorination of citrus-derived limonene [1]. Carvone contains three reducible functionalities, a carbonyl group and an endo- and exo-cyclic -CH=CH-. Reaction of carvone with hydrogen generates valuable chemicals (**Figure 1**) in the pharmaceutical, food and agriculture sectors [2]. Reaction selectivity is challenging and most methodologies are non-selective, generating product mixtures [3-6]. Current carvacrol production includes (i) supercritical (300 bar) CO<sub>2</sub> extraction from oregano essential oils [7] and (ii) industrial scale isopropylation of *o*-cresol with propylene over activated alumina at 633 K and 50 bar [8]. The requirements for high operating pressures and temperatures (>523 K) are major drawbacks. Application of supported metal catalysts to promote carvone → carvacrol (in H<sub>2</sub>) is an alternative but studies to date are sparse and inconclusive with work focused on batch systems in organic solvents (*e.g.* toluene, hexane, alcohols) [3,6,9-13]. Solvent-free continuous processing at atmospheric pressure offers advantages in terms of throughput and sustainability. The carvone → carvacrol reaction mechanism is still a matter of debate. Klabunovskii *et al.* [13] proposed a classical Horiuti-Polanyi mechanism for reaction over Pd with carvotanacetone as reaction intermediate (**Figure 1**, path **IA**). Supported Pt catalysts do not promote carvacrol formation [3,10-12] and selectivities reported for the most selective Pd catalysts [13,14] are low (≤38%).

The redox and acid-base properties of the metal support can influence catalytic activity/selectivity in the reduction of carbonyl and/or unsaturated groups where stronger -C=O (*vs.* -CH=CH-) polarisation on surface Lewis acid sites promotes unsaturated alcohols [15]. Preferential carbonyl and -CH=CH- reduction has been reported over Pd on reducible (CeO<sub>2</sub>, TiO<sub>2</sub>) [16] and non-reducible (Al<sub>2</sub>O<sub>3</sub>) oxides [17], respectively. In this study we set out to identify the critical variable(s) that control carvone → carvacrol by examining

commercial and laboratory-synthesised Pd catalysts. We compare the catalytic action of (unsupported) bulk Pd with Pd on (non-reducible Al<sub>2</sub>O<sub>3</sub> and reducible CeO<sub>2</sub>) oxides and carbon. We evaluate the effect of H<sub>2</sub> content in the feed as a critical process variable.

## 2 Experimental

### 2.1 Catalyst Preparation and Activation

Ceria, 1.2% wt. Pd/Al<sub>2</sub>O<sub>3</sub>, 1.1% wt. Pd/C and PdO were obtained from Sigma-Aldrich. Synthesis of Pd/CeO<sub>2</sub> by deposition-precipitation followed a prior procedure [18]. Samples were sieved to mean diameter = 75 μm, activated in 60 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> at 10 K min<sup>-1</sup> to 573 K and passivated in 1% v/v O<sub>2</sub>/He at ambient temperature prior to *ex-situ* characterisation.

### 2.2 Catalyst Characterisation

Palladium content was measured by ICP-OES (Vista-Pro, Varian Inc.). Catalyst activation by temperature programmed reduction (TPR, in 5% v/v H<sub>2</sub>/N<sub>2</sub> at 10 K min<sup>-1</sup> to 573 K), H<sub>2</sub> (at 423 K) and O<sub>2</sub> (at ambient temperature) chemisorption and total specific surface area (SSA, in 30% v/v N<sub>2</sub>/He using the single point BET method) measurements were conducted on the commercial CHEM-BET 3000 (Quantachrome) unit as described elsewhere [19]; results were reproducible to ±7%. Palladium particle morphology was determined by scanning transmission electron microscopy (STEM, JEOL 2200FS field emission gun-equipped TEM), employing Gatan Digital Micrograph 1.82 for data acquisition/manipulation. Samples for analysis were crushed and deposited (dry) on a holey carbon/Cu grid (300 Mesh). Surface area-weighted mean Pd sizes ( $d_{STEM}$ ) were determined from a count of 800 particles [19]. Metal size for bulk Pd was determined by H<sub>2</sub> chemisorption [20].

## 2.3 Catalytic Procedure

### 2.3.1 Materials

Carvone (98%), carvacrol (98%), dihydrocarvone (99%) and carveol (98%) were obtained from Sigma-Aldrich. Carvotanacetone, carvomenthone and carvomenthol were synthesised following published methods [21]. All gases (H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and He) were ultra-high purity (BOC, 99.9%).

### 2.3.2 Catalytic System

Reactions were conducted at atmospheric pressure and isothermal conditions (423 K) *in situ* after activation in a continuous flow fixed bed vertical tubular glass reactor (15 mm i.d.). A layer of borosilicate glass beads served as preheating zone where the organic reactant was vaporised and reached reaction temperature before contacting the catalyst. Temperature was continuously monitored by a thermocouple inserted in a thermowell within the catalyst bed. The organic reactant was delivered *via* a glass/teflon air-tight syringe and teflon line using a microprocessor controlled infusion pump (Model 100 kd Scientific) at a fixed calibrated flow rate. A co-current flow of N<sub>2</sub>, H<sub>2</sub> or H<sub>2</sub>+N<sub>2</sub> with carvone (N<sub>2</sub>/Carvone = 20/1 mol mol<sup>-1</sup>, H<sub>2</sub>/Carvone = 1/6 – 20/1 mol mol<sup>-1</sup>) was maintained at **gas hourly space velocity** (*GHSV*) = 2 × 10<sup>4</sup> – 1 × 10<sup>5</sup> h<sup>-1</sup>. Palladium (*n*) to reactant (*F*) molar ratio spanned the range 1 × 10<sup>-5</sup> – 5 × 10<sup>-2</sup> h. In blank tests, reactions in the absence of catalyst did not result in any measurable conversion. The reactor effluent was frozen in a liquid N<sub>2</sub> trap for analysis using a Perkin-Elmer Auto System XL gas chromatograph with split/splitless injector, FID and Stabilwax capillary column (RESTEK). Data acquisition/manipulation used the TotalChrom data system. Fractional carvone conversion (*X*) is given by:

$$X = \frac{[\text{Carvone}]_{\text{in}} - [\text{Carvone}]_{\text{out}}}{[\text{Carvone}]_{\text{in}}} \quad (1)$$

with selectivity to carvacrol (*S*<sub>Carvacrol</sub>):

$$S_{\text{Carvacrol}} (\%) = \frac{[\text{Carvacrol}]_{\text{out}}}{[\text{Carvone}]_{\text{in}} - [\text{Carvone}]_{\text{out}}} \times 100 \quad (2)$$

and yield ( $Y_{\text{Carvacrol}}$ ):

$$Y_{\text{Carvacrol}} (\%) = X \times S_{\text{Carvacrol}} \quad (3)$$

Catalytic activity is also quantified in terms of reactant consumption rate ( $R$ ,  $\text{mol}_{\text{Carvone}} \text{mol}_{\text{Pd}}^{-1} \text{s}^{-1}$ ), extracted from time on-stream measurements [22]. Turnover frequency (TOF, rate per active site) was determined from particle size measurements [22]. Repeated reactions with different samples from the same batch of catalyst delivered raw data reproducibility and carbon mass balances within  $\pm 5\%$ .

### 3 Results and Discussion

#### 3.1 Catalyst Characterisation

Physicochemical properties of the catalysts in this study are given in **Table 1**. The commercial and laboratory synthesised samples display a range of SSA ( $3\text{-}870 \text{ m}^2 \text{ g}^{-1}$ ). The TPR profiles (**Figure 2**) exhibit a negative peak ( $\text{H}_2$  release) at  $350\text{-}383 \text{ K}$  due to decomposition of Pd hydride formed by  $\text{H}_2$  adsorption at ambient temperature [20]. The lower hydride Pd/H ratio for supported ( $0.06\text{-}0.04$ ) relative to bulk Pd ( $0.67$ ) is consistent with nano-scale metal particles as is the shift to lower decomposition temperatures [20]. TPR of Pd/ $\text{CeO}_2$  (**Figure 2(IV)**) presents a positive peak at the final isothermal hold ( $573 \text{ K}$ ), suggesting partial  $\text{CeO}_2$  reduction (at the metal-support interface) with the formation of oxygen vacancies [23]. This was confirmed by  $\text{O}_2$  titration post-TPR where  $\text{O}_2$  uptake ( $160 \mu\text{mol g}^{-1}$ ) is comparable with values in the literature [24]. Hydrogenation performance is determined by the capacity of Pd for  $\text{H}_2$  adsorption/dissociation [20]. Hydrogen chemisorption at reaction temperature (**Table 1**) was close to detection limits for bulk Pd and appreciably lower than that recorded for the supported systems. Uptake was equivalent for Pd/ $\text{Al}_2\text{O}_3$  and Pd/C and measurably higher for Pd/ $\text{CeO}_2$ . Differences in  $\text{H}_2$  chemisorption can

be due to variations in metal dispersion [19]. The three supported catalysts present pseudo-spherical Pd particles in the 1-6 nm range (Figure 3(I)) with a similar size distribution (Figure 3(II)) and mean ( $d_{STEM} \sim 3$  nm, Table 1). Greater H<sub>2</sub> chemisorption on Pd/CeO<sub>2</sub> can be linked to partial support reduction with the generation of sites for H<sub>2</sub> adsorption. Wang *et al.* [25] have recently discussed the formation of active sites at the interface of metal nanoparticles strongly interacting with reducible CeO<sub>2</sub>. Tu and Cheng [26] reported a synergistic effect between Pd and CeO<sub>2</sub> that resulted in stronger H<sub>2</sub> adsorption and increased uptake.

### 3.2 Gas Phase Conversion of Carvone

Reaction thermodynamics establishes greater stability of conjugated endo-cyclic -CH=CH- and carbonyl functionalities in carvone [27] with the following order of decreasing reactivity based on Gibbs free energy [28]: exo -CH=CH- > endo -CH=CH- > -C=O. This can account for the reported formation of unsaturated and saturated ketones (Figure 1 (path (II))) as principal products in the hydrogenation of carvone [6]. Variations in H<sub>2</sub> content in the feed (represented as inlet H<sub>2</sub>/Carvone) were tested in order to probe reaction pathway. A range of H<sub>2</sub>/Carvone ratios was considered, from 0 (reaction in N<sub>2</sub>) to sub- (H<sub>2</sub>/Carvone = 1/6), stoichiometric (= 1/1) and H<sub>2</sub> in excess (= 20/1) for the reduction of a single carvone functionality. Under all reaction conditions, formation of dihydrocarvone (endo -CH=CH- reduction, path (III)) and carvomenthol (-C=O reduction in carvomenthone, path (II)) was negligible with selectivities  $\leq 6\%$ .

Reaction in N<sub>2</sub> did not result in any measurable conversion of carvone. Under hydrogen lean conditions (H<sub>2</sub>/Carvone = 1/6), we achieved full selectivity to the target carvacrol for reaction over bulk Pd, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/C (Table 1 and Figure 4(I)). This result is significant given the reports in batch liquid phase carvone hydrogenation where low selectivity to carvacrol ( $\leq 38\%$ ) was obtained over unsupported Pd [13] and (C and Al<sub>2</sub>O<sub>3</sub>) supported Pd



[13,14]. Variations in contact time can govern selectivity [29] and the exclusivity to carvacrol achieved in this study may result from the lower contact time (0.03-0.2 s) in continuous operation. Negligible conversion of carvotanacetone was recorded for reactions in N<sub>2</sub> or H<sub>2</sub> lean conditions. This indicates direct carvacrol formation from carvone *via* hydrogen migration and keto-enol tautomerisation, following path **(IB)** in **Figure 1**. Catalytic inactivity for carvone reaction in N<sub>2</sub> suggests that carvacrol formation requires H<sub>2</sub> in the feed. This is in line with recent work by Zhang *et al.* [30] who reported formation of phenols over Pd/C *via* hydrogen treatment of substituted 2-cyclohexenones. Naito and Tanimoto [31] provided direct evidence for intramolecular double-bond migration in propene hydrogenation over Pd/SiO<sub>2</sub> while Musolino *et al.* [32] established a hydrogen requirement for double bond migration in *cis*-2-butene-1,4-diol → 2-hydroxytetrahydrofuran transformation over Pd/C.

Pd/CeO<sub>2</sub> exhibited different behaviour in promoting carveol formation (*S* = 10%) *via* -C=O hydrogenation (path **(IV)** in **Figure 1**). This can be attributed to the involvement of surface oxygen vacancies where the carbonyl group is activated at Ce<sup>3+</sup> sites for hydrogen attack to generate carveol. Neri *et al.* [16] proposed preferential formation of an unsaturated alcohol from an unsaturated aldehyde over Pd on reducible oxides (TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>), which they ascribed to reactant activation on the support. Calaza *et al.* [33] demonstrated (by TPD, RAIRS and DFT) carbonyl activation at oxygen vacancies on CeO<sub>2</sub>. We observed an initial decline in conversion that attained steady state for all the systems (see inset to **Figure 4(I)** for Pd/Al<sub>2</sub>O<sub>3</sub>). Similar reaction rates (and *TOF*) were obtained for the three supported Pd catalysts, which were appreciably greater than bulk Pd (**Table 1**) and can be linked to H<sub>2</sub> uptake capacity under reaction conditions. At an inlet H<sub>2</sub>/Carvone = 1/6, carvacrol yield was proportional to Pd content (**Figure 4(II)**) to reach 100% in the case of Pd, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/C. The lower yield over Pd/CeO<sub>2</sub> was due to carveol formation. An increase in H<sub>2</sub>/Carvone resulted in decreased carvacrol selectivity where the data for all the catalysts

converged on a common trend line (**Figure 4(I)**). Loss of carvacrol selectivity with increasing H<sub>2</sub> content was accompanied by formation of carvotanacetone and carvomenthone, which were promoted at higher H<sub>2</sub>/Carvone (**Table 1**). Olefin conversion over transition metal catalysts proceeds through an allyl intermediate that is formed by a hydrogen addition [34]. This intermediate can undergo (i) H elimination with bond migration or (ii) insertion of a second H to generate the alkane [34]. The switch from double bond migration (path **(IB)** in **Figure 1**) to hydrogenation (path **(II)**) is sensitive to H<sub>2</sub>/Carvone, which is consistent with the literature [32]. Hydrogen elimination is favoured under conditions of low surface hydrogen (H<sub>2</sub>/Carvone = 1/6). Increased H<sub>2</sub> content facilitates H insertion, directing the reaction to preferential hydrogenation. Carveol formation over Pd/CeO<sub>2</sub> was insensitive to H<sub>2</sub>/Carvone.

#### 4 Conclusions

We have established exclusive formation of carvacrol at full carvone conversion over Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/C (mean Pd size = 2.8-3.0 nm) at an inlet H<sub>2</sub>/Carvone = 1/6. Under the same reaction conditions, bulk Pd with lower H<sub>2</sub> uptake capacity delivered 100% carvacrol yield at a lower rate. Reaction over Pd/CeO<sub>2</sub> promoted formation of carveol due to -C=O activation at oxygen vacancies created during TPR. Hydrogenation to carvotanacetone and carvomenthone was promoted at higher H<sub>2</sub>/Carvone (>1/6).

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**Table 1:** Palladium content, specific surface area (SSA), H<sub>2</sub> chemisorption (at 423 K), mean Pd size ( $d_{\text{STEM}}$ ), carvone consumption rate ( $R$ ) and turnover frequency ( $TOF$ ) and carvacrol, carvotanacetone and carvomenthone selectivity ( $S_{\text{Product}}$ ) at  $X \sim 0.3$  for different inlet H<sub>2</sub>/Carvone.

Catalyst	Pd content (% wt.)	SSA (m <sup>2</sup> g <sup>-1</sup> )	H <sub>2</sub> uptake (mmol g <sub>Pd</sub> <sup>-1</sup> )	$d_{\text{STEM}}$ (nm)	H <sub>2</sub> /Carvone = 1/6		$S_{\text{Carvotanacetone}}/S_{\text{Carvomenthone}}$ (%)		
					$R$ (mol <sub>Carvone</sub> mol <sub>Pd</sub> <sup>-1</sup> s <sup>-1</sup> ) / $TOF$ (s <sup>-1</sup> )	$S_{\text{Carvacrol}}$ (%)	H <sub>2</sub> /Carvone		
							1/1	5/1	10/1
Pd	-	3	<0.04	-	$1.4 \times 10^{-3}$ / 0.2 <sup>a</sup>	100	30/0	29/13	28/14
Pd/Al <sub>2</sub> O <sub>3</sub>	1.2	145	1.7	3.0	2.3 / 6.2	100	12/1	15/4	21/8
Pd/C	1.1	870	2.0	2.8	2.3 / 5.7	100	13/1	17/2	27/7
Pd/CeO <sub>2</sub>	0.5	37	9.0	3.0	2.5 / 6.7	90	13/0	18/2	24/3

<sup>a</sup> $TOF$  obtained using Pd size (=130 nm) from H<sub>2</sub> chemisorption (see Experimental section).

## Figure captions

**Figure 1:** Reaction pathways in the conversion of carvone to (target) carvacrol (**path I**, solid arrows), carvomenthol (**path II**, open arrows), dihydrocarvone (**path III**, dashed arrow) and carveol (**path IV**, dotted arrow).

**Figure 2:** Temperature programmed reduction (TPR) profiles for **(I)** PdO, **(II)** Pd/Al<sub>2</sub>O<sub>3</sub>, **(III)** Pd/C and **(IV)** Pd/CeO<sub>2</sub>.

**Figure 3:** **(I)** Representative STEM image with **(II)** Pd size histogram for **(A)** Pd/Al<sub>2</sub>O<sub>3</sub>, **(B)** Pd/C and **(C)** Pd/CeO<sub>2</sub>.

**Figure 4:** **(I)** Effect of inlet H<sub>2</sub>/Carvone on selectivity to carvacrol ( $S_{\text{Carvacrol}}$ ). *Inset: variation of carvone fractional conversion ( $X$ ) with time on-stream over Pd/Al<sub>2</sub>O<sub>3</sub> (■);* **(II)** variation of carvacrol yield ( $Y_{\text{Carvacrol}}$ ) with Pd content in the catalyst bed ( $n$ ) for reaction over Pd (★), Pd/Al<sub>2</sub>O<sub>3</sub> (□), Pd/C (△) and Pd/CeO<sub>2</sub> (○). *Note: Bottom  $x$ -coordinate in (II) refers to Pd (★). Reaction conditions:  $T = 423$  K, H<sub>2</sub>/Carvone = 1/6 – 20/1,  $n/F = 1 \times 10^{-5} - 5 \times 10^{-2}$  h,  $GHSV = 2 \times 10^4 - 1 \times 10^5$  h<sup>-1</sup>.*

Figure 1

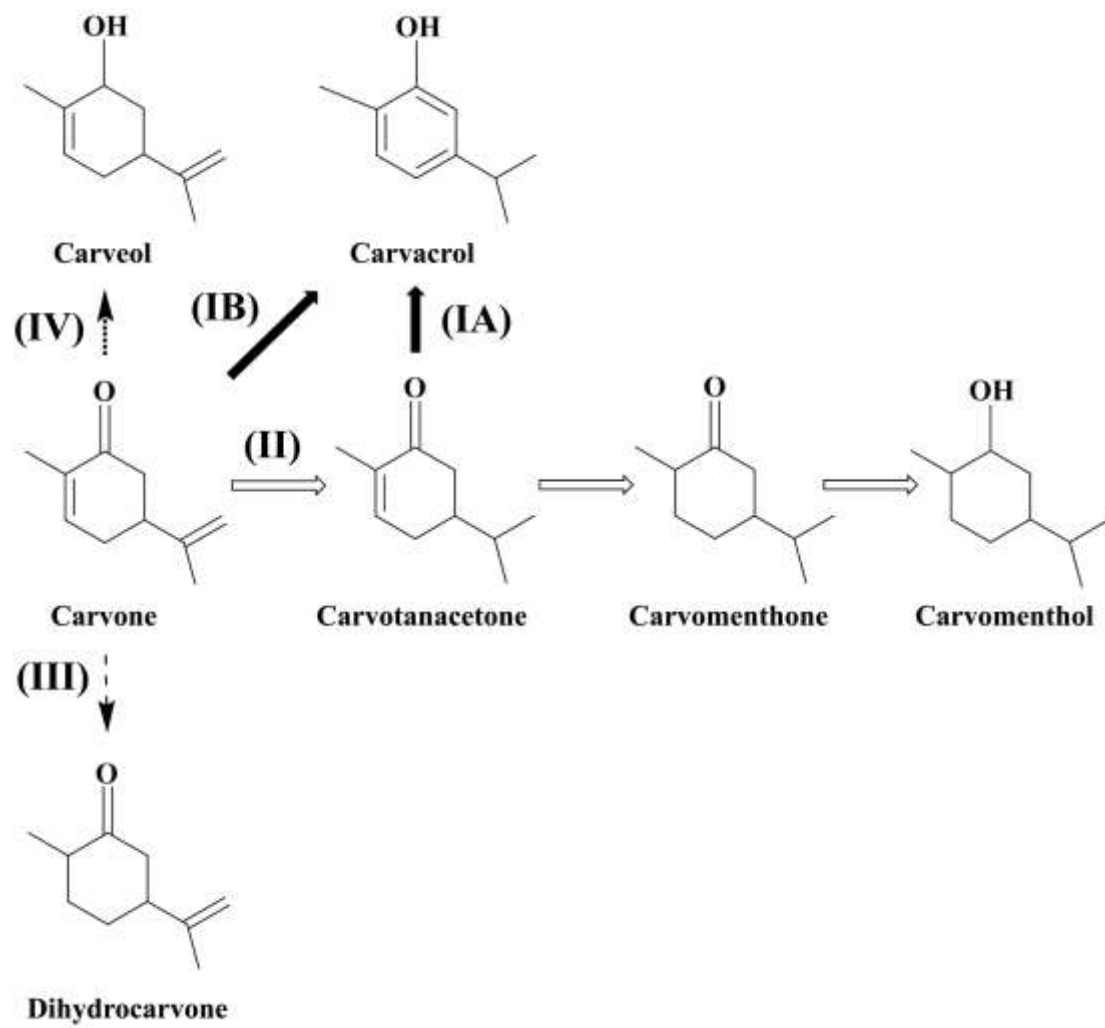
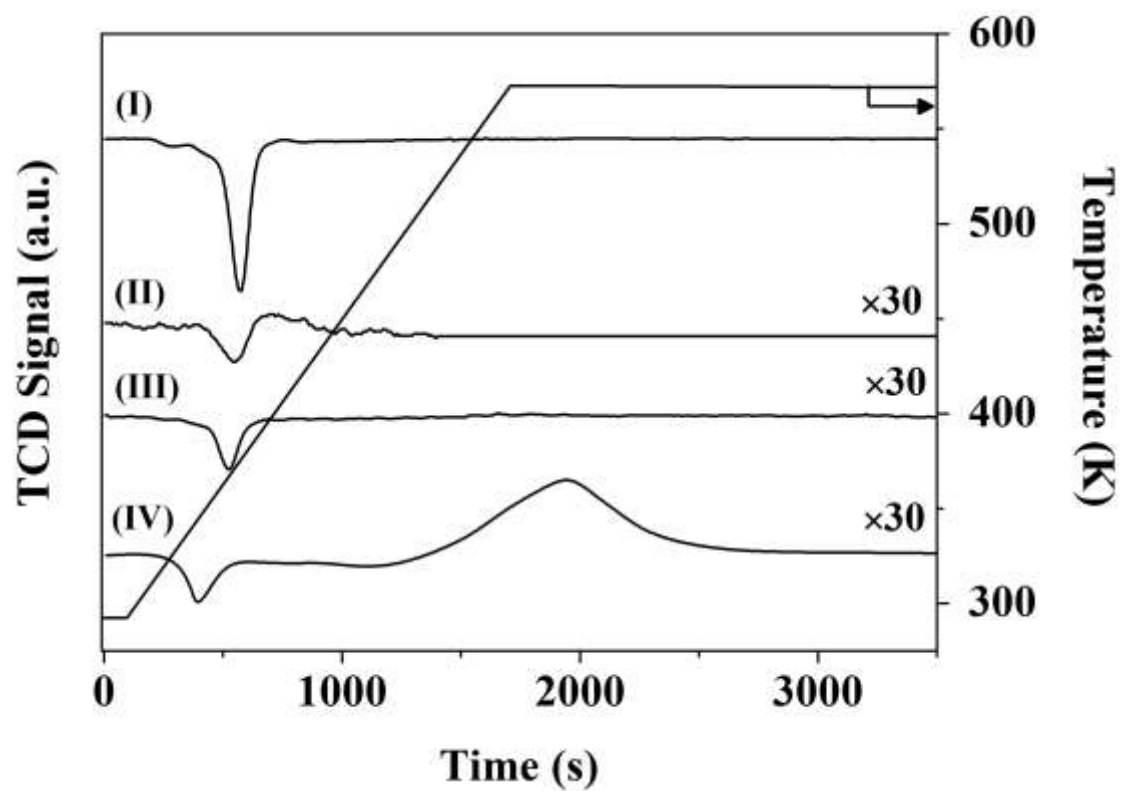


Figure 2





**Figure 3**

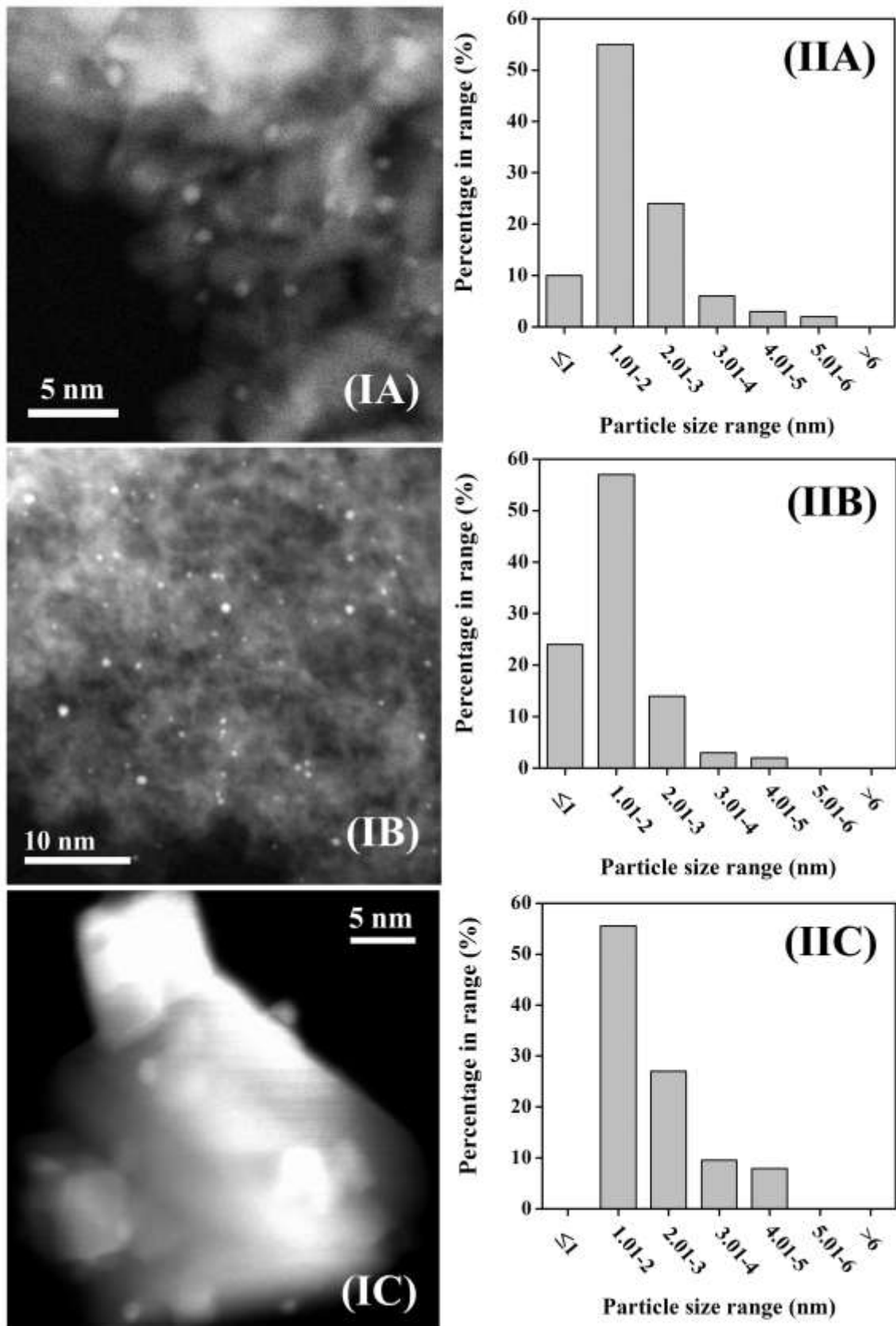


Figure 4

