

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

Pedro Benavente,

Fernando Cárdenas-Lizana* and Mark A. Keane

**Chemical Engineering, School of Engineering and Physical Sciences,
Heriot-Watt University, Edinburgh EH14 4AS, Scotland**

*corresponding author: tel.: +44(0)131 4514115,
e-mail: F.CardenasLizana @hw.ac.uk

Abstract

The selective conversion of biomass-derived carvone in H₂ was studied over (Al₂O₃, C and CeO₂) supported Pd (mean size 2.8-3.0 nm), taking bulk Pd as benchmark. 100% carvacrol yield was achieved over Pd/Al₂O₃, Pd/C and bulk Pd at an inlet H₂/Carvone = 1/6, with appreciably higher rates for the supported catalysts. Carveol formation over Pd/CeO₂ was attributed to -C=O activation at surface oxygen vacancies (confirmed by O₂ titration) generated during TPR. Carvotanacetone and carvomenthone formation were observed at H₂/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) CO₂ 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 H₂) 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 (CeO₂, TiO₂) [16] and non-reducible (Al₂O₃) 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 Al₂O₃ and reducible CeO₂) oxides and carbon. We evaluate the effect of H₂ content in the feed as a critical process variable.

2 Experimental

2.1 Catalyst Preparation and Activation

Ceria, 1.2% wt. Pd/Al₂O₃, 1.1% wt. Pd/C and PdO were obtained from Sigma-Aldrich. Synthesis of Pd/CeO₂ by deposition-precipitation followed a prior procedure [18]. Samples were sieved to mean diameter = 75 μm, activated in 60 cm³ min⁻¹ H₂ at 10 K min⁻¹ to 573 K and passivated in 1% v/v O₂/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 H₂/N₂ at 10 K min⁻¹ to 573 K), H₂ (at 423 K) and O₂ (at ambient temperature) chemisorption and total specific surface area (SSA, in 30% v/v N₂/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 H₂ 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 (H₂, N₂, O₂ 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 N₂, H₂ or H₂+N₂ with carvone (N₂/Carvone = 20/1 mol mol⁻¹, H₂/Carvone = 1/6 – 20/1 mol mol⁻¹) was maintained at **gas hourly space velocity** (*GHSV*) = 2 × 10⁴ – 1 × 10⁵ h⁻¹. Palladium (*n*) to reactant (*F*) molar ratio spanned the range 1 × 10⁻⁵ – 5 × 10⁻² 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 N₂ 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*_{Carvacrol}):

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

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 (H_2 release) at $350\text{-}383 \text{ K}$ due to decomposition of Pd hydride formed by 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/ CeO_2 (**Figure 2(IV)**) presents a positive peak at the final isothermal hold (573 K), suggesting partial CeO_2 reduction (at the metal-support interface) with the formation of oxygen vacancies [23]. This was confirmed by O_2 titration post-TPR where 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 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/ Al_2O_3 and Pd/C and measurably higher for Pd/ CeO_2 . Differences in 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 H₂ chemisorption on Pd/CeO₂ can be linked to partial support reduction with the generation of sites for H₂ adsorption. Wang *et al.* [25] have recently discussed the formation of active sites at the interface of metal nanoparticles strongly interacting with reducible CeO₂. Tu and Cheng [26] reported a synergistic effect between Pd and CeO₂ that resulted in stronger H₂ 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 H₂ content in the feed (represented as inlet H₂/Carvone) were tested in order to probe reaction pathway. A range of H₂/Carvone ratios was considered, from 0 (reaction in N₂) to sub- (H₂/Carvone = 1/6), stoichiometric (= 1/1) and H₂ 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 N₂ did not result in any measurable conversion of carvone. Under hydrogen lean conditions (H₂/Carvone = 1/6), we achieved full selectivity to the target carvacrol for reaction over bulk Pd, Pd/Al₂O₃ 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 Al₂O₃) 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 N₂ or H₂ 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 N₂ suggests that carvacrol formation requires H₂ 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/SiO₂ 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/CeO₂ 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 Ce³⁺ 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 (TiO₂, ZnO, Fe₂O₃), 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 CeO₂. We observed an initial decline in conversion that attained steady state for all the systems (see inset to **Figure 4(I)** for Pd/Al₂O₃). 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 H₂ uptake capacity under reaction conditions. At an inlet H₂/Carvone = 1/6, carvacrol yield was proportional to Pd content (**Figure 4(II)**) to reach 100% in the case of Pd, Pd/Al₂O₃ and Pd/C. The lower yield over Pd/CeO₂ was due to carveol formation. An increase in H₂/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 H₂ content was accompanied by formation of carvotanacetone and carvomenthone, which were promoted at higher H₂/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 H₂/Carvone, which is consistent with the literature [32]. Hydrogen elimination is favoured under conditions of low surface hydrogen (H₂/Carvone = 1/6). Increased H₂ content facilitates H insertion, directing the reaction to preferential hydrogenation. Carveol formation over Pd/CeO₂ was insensitive to H₂/Carvone.

4 Conclusions

We have established exclusive formation of carvacrol at full carvone conversion over Pd/Al₂O₃ and Pd/C (mean Pd size = 2.8-3.0 nm) at an inlet H₂/Carvone = 1/6. Under the same reaction conditions, bulk Pd with lower H₂ uptake capacity delivered 100% carvacrol yield at a lower rate. Reaction over Pd/CeO₂ promoted formation of carveol due to -C=O activation at oxygen vacancies created during TPR. Hydrogenation to carvotanacetone and carvomenthone was promoted at higher H₂/Carvone (>1/6).

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Table 1: Palladium content, specific surface area (SSA), H₂ chemisorption (at 423 K), mean Pd size (d_{STEM}), carvone consumption rate (R) and turnover frequency (TOF) and carvacrol, carvotanacetone and carvomenthone selectivity (S_{Product}) at $X \sim 0.3$ for different inlet H₂/Carvone.

Catalyst	Pd content (% wt.)	SSA (m ² g ⁻¹)	H ₂ uptake (mmol g _{Pd} ⁻¹)	d_{STEM} (nm)	H ₂ /Carvone = 1/6		$S_{\text{Carvotanacetone}}/S_{\text{Carvomenthone}}$ (%)		
					R (mol _{Carvone} mol _{Pd} ⁻¹ s ⁻¹) / TOF (s ⁻¹)	$S_{\text{Carvacrol}}$ (%)	H ₂ /Carvone		
							1/1	5/1	10/1
Pd	-	3	<0.04	-	1.4×10^{-3} / 0.2 ^a	100	30/0	29/13	28/14
Pd/Al ₂ O ₃	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 ₂	0.5	37	9.0	3.0	2.5 / 6.7	90	13/0	18/2	24/3

^a TOF obtained using Pd size (=130 nm) from H₂ 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/Al₂O₃, **(III)** Pd/C and **(IV)** Pd/CeO₂.

Figure 3: **(I)** Representative STEM image with **(II)** Pd size histogram for **(A)** Pd/Al₂O₃, **(B)** Pd/C and **(C)** Pd/CeO₂.

Figure 4: **(I)** Effect of inlet H₂/Carvone on selectivity to carvacrol ($S_{\text{Carvacrol}}$). *Inset: variation of carvone fractional conversion (X) with time on-stream over Pd/Al₂O₃ (■);* **(II)** variation of carvacrol yield ($Y_{\text{Carvacrol}}$) with Pd content in the catalyst bed (n) for reaction over Pd (★), Pd/Al₂O₃ (□), Pd/C (△) and Pd/CeO₂ (○). *Note: Bottom x-coordinate in (II) refers to Pd (★). Reaction conditions: $T = 423$ K, H₂/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⁻¹.*

Figure 1

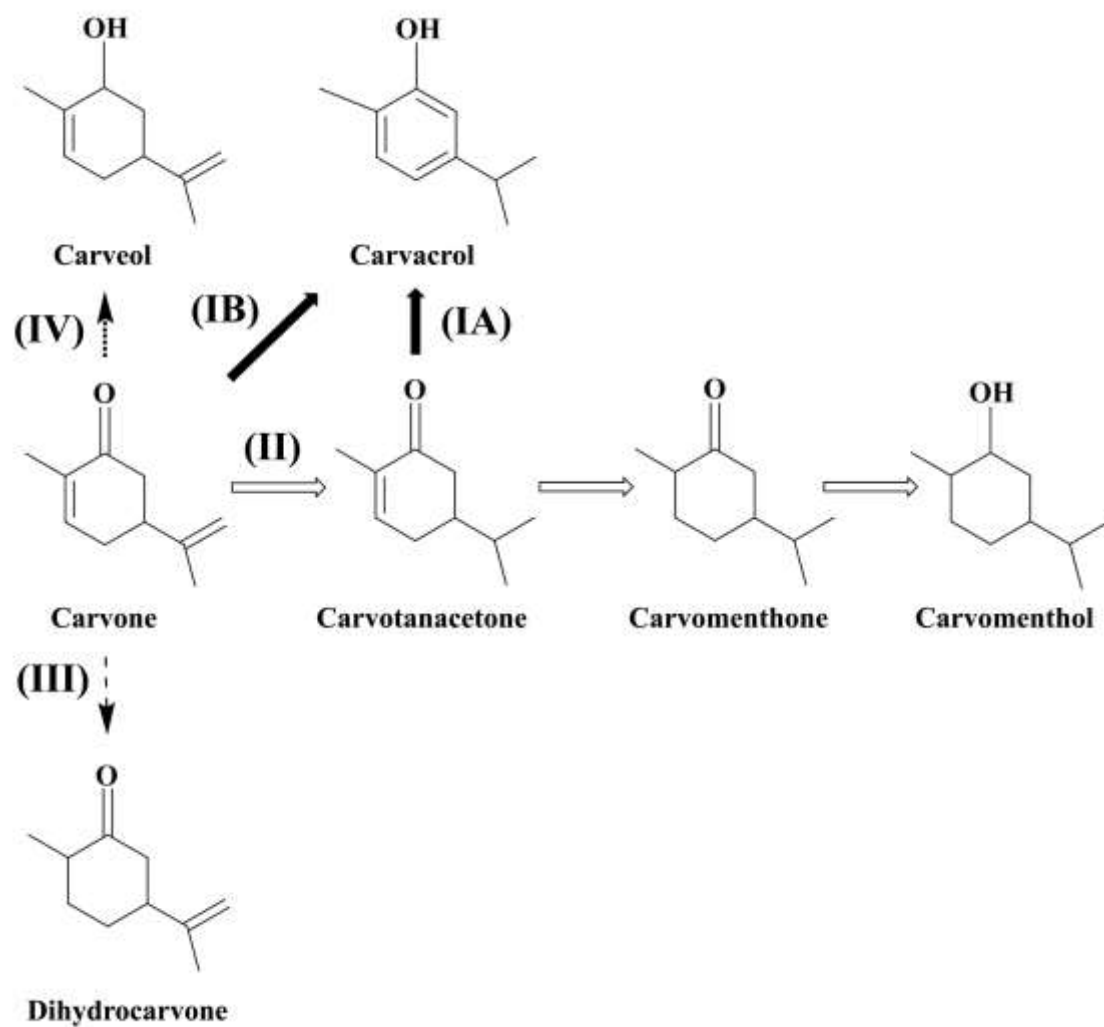


Figure 2

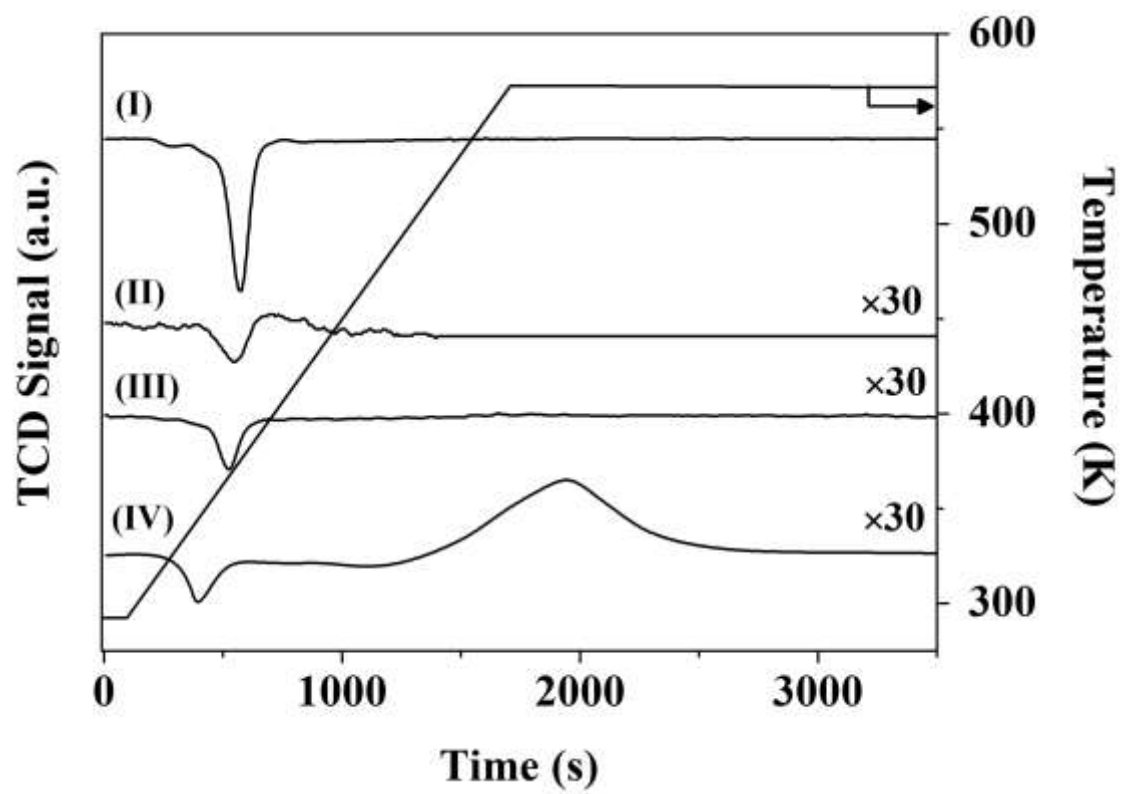


Figure 3

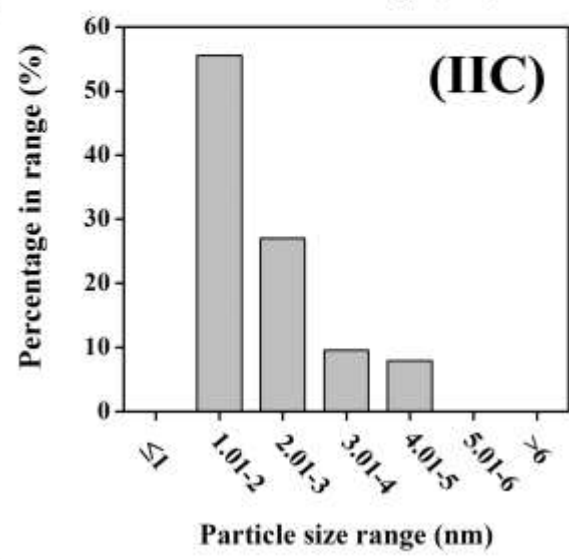
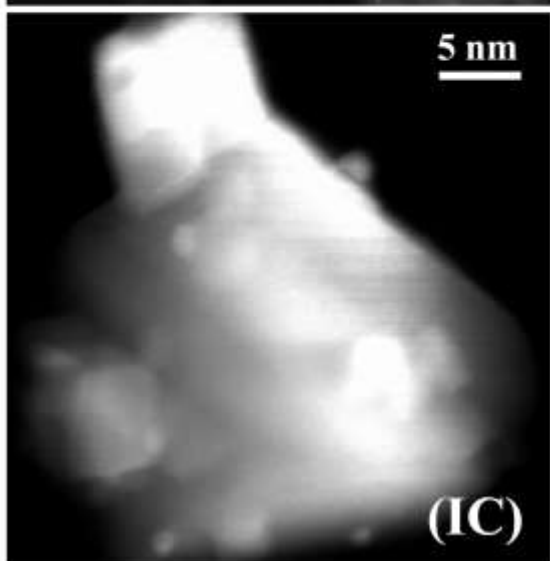
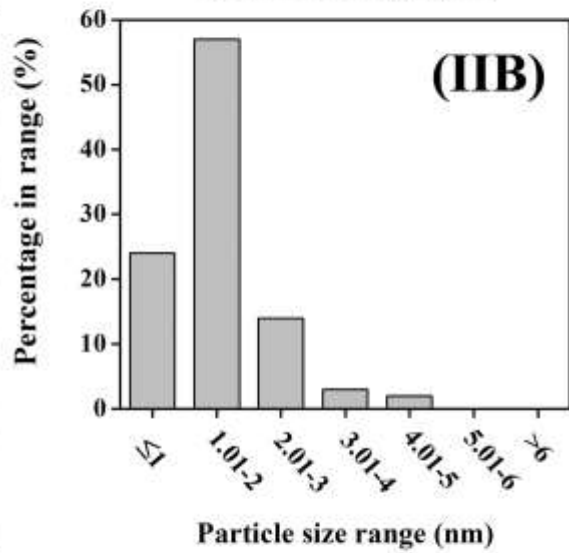
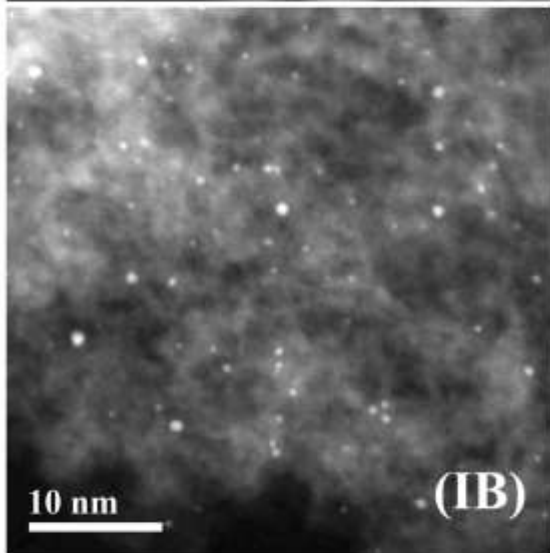
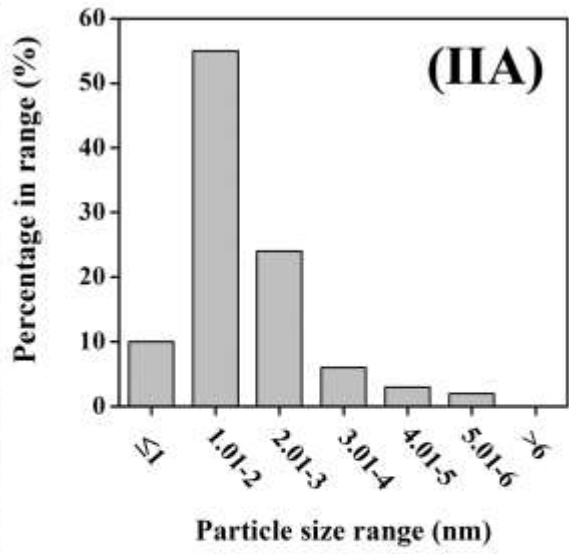
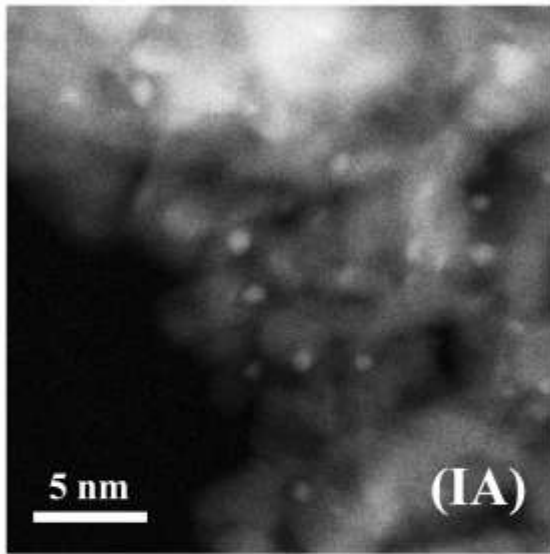


Figure 4

