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Pt and Pt/Sn carbonyl clusters as precursors for the synthesis of supported metal catalysts for the base-free oxidation of HMF

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Graphical Abstract



- Pt-based carbonyl clusters are suitable precursor for small Pt NPs
- Cluster derived materials are effective in base-free HMF oxidation
- Sn addition enhances catalyst activity and stability

Abstract

In the present work, Pt and Pt/Sn nanoparticles (NPs), synthesized from carbonyl cluster precursors were deposited on TiO₂ and the resulting materials were tested as catalysts in selective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA). The work was mainly focused on the study of the formation of bimetallic or mixed oxide-metal nanoparticles on

TiO₂ starting with Pt/Sn carbonyl clusters and on the structure-activity relationship in the reaction of HMF oxidation in base-free conditions. The developed synthesis procedure allowed to obtain very small mono and bimetallic particles characterized by a narrow particle size distribution. Promising results in base-free FDCA production have been achieved using the prepared samples. In particular, the introduction of Sn in an equimolar amount with Pt improved the catalyst activity as well as its time stability upon operation, demonstrating that the modification of Pt electronic configuration by Sn is a key factor for the mastering of functional performances.

Keywords carbonyl cluster, Pt/Sn, 5-hydroxymethylfurfural oxidation, 2,5-furandicarboxylic acid

1 Introduction

The conversion of biomass derived molecules for the development of new processes with low environmental impact is an appealing topic both from a fundamental and applied perspective. Within this field, 5-hydroxymethylfurfural (HMF), obtained by renewable biomasses, is one of the most studied platform molecules for the sustainable production of various fuels and chemicals. [1-7]. The presence of different functional groups such as hydroxyl, formyl and furan rings enhance HMF reactivity, allowing different reactions such as reduction, oxidation and esterification to take place. Over the past two decades, HMF oxidation has been widely studied using different reaction conditions and heterogeneous catalysts with specific metal content and morphology.[7-11] Selective oxidation of this molecule leads to the formation of 2,5-furandicarboxylic acid (FDCA), which is one of the most promising intermediates for the production of poly(ethylene furanoate) (PEF), the furan-based analogue to poly(ethylene terephthalate) (PET), which is the dominant polymer in the beverage packaging industries. Recently, it has been reported that the 100% bio-based polymer made up of FDCA and bio-sourced ethylene glycol is characterised by reduced oxygen and carbon dioxide permeability compared to PET.[12, 13] Moreover, many companies are genuinely interested in developing processes for FDCA production as a possible candidate monomer for the synthesis of polyesters, polyamides and polyurethanes. Consequently, several patents have been published in this field.[14-17]

In the last few years, a number of pilot scale plants have also been developed for the current process, such as Du Pont[18] and Synvina,[19] however, technical problems have been reported for the final commercialisation of the process. Nevertheless, the optimized route for the synthesis of FDCA has not yet been identified and the current technology for terephthalic acid production using metal/bromide catalysts seems to be currently used in pilot reactor, to facilitate is direct integration

into existing terephthalic acid production lines.[20] One drawback of these catalytic systems is the use of corrosive media and dangerous compounds, which make the process polluting. Thus, the commercially viable production of FDCA has not yet realized.

Currently, the recent focus is on the search for efficient catalysts and process condition to prepare FDCA in aqueous media and as a consequence, the preparation of active and stable supported metal catalysts, eventually combining two metals for improving activity, selectivity and long-term stability, is attracting a great interest.[21, 22] In this regard, Pt[8, 23-27] is one of the most commonly used metals, together with Au[28-32] and Pd.[33-36]

Moreover, the tailoring of metal nanoparticle morphology for the preparation of mono and bimetallic systems, in terms of nanoparticle size and shape, and structure (alloy versus core-shell bimetallic systems) can be a useful tool to improve catalyst activity, minimising leaching, poisoning and therefore enhancing long term stability. Recent studies have reported that Au/Cu,[37-39] Au/Pd [40-47] bimetallic nanoparticles either in the form of alloy or as core-shell structure were active in HMF selective oxidation, showing superior catalytic performance with respect to their monometallic counterparts. However, the necessity of basic conditions to activate and stabilize these catalysts is still the main concern from the industrial point of view. Remarkable results in base-free FDCA production have been achieved by Ebitani and coworkers[48] using Pd/Pt bimetallic nanoparticles supported on hydrotalcite. Nevertheless, the potential contribution of solubilized inorganic basic support and concerns on catalyst stability remain hotly debated.

Recently, bimetallic Pt/Sn supported catalysts attracted renewed interest since they exhibit high activity and stability in liquid phase hydrogenation and oxidation of biomass-derived molecules.[49-52]. The addition of Sn to Pt seems to lead to the formation of unique active sites and the different formed phases were demonstrated to facilitate different reactions. As an example, Zhao and co-workers, demonstrated that the synergy between Pt and Sn species was remarkable and resulted in excellent activity in the acetic acid hydrogenation and ethanol selectivity [50] while Davis and co-workers [49] studied the aqueous phase oxidation of 1,6-hexanediol using a series of carbon-supported Pt/Sn materials and proved the importance of the formed species on the oxidation activity.

On the bases of this information the use of bimetallic Pt/Sn catalysts with controlled particle size and metal composition may be a promising way to improve catalyst activity and stability in the basefree oxidation of HMF.

Pt/Sn catalysts are generally prepared by impregnation method, leading to a quite limited control of the structural parameters, while the use of molecular metal clusters has been reported to be a suitable methodology for the synthesis of well defined nanosystems,[53-55] and thus, it could be considered as well a promising route for the synthesis of well-defined Pt/Sn systems with controlled

metal composition, particle size and structure, as also reported for other supported bimetallic nanoparticles.[56-60]

In view of the above considerations, the present work has focused on the synthesis and characterization of TiO₂-supported Pt and Pt/Sn nanoparticles obtained from carbonyl cluster decomposition. The described synthetic route has not investigated so far for the designing of Pt-based nanoparticles for the oxidation of HMF. In particular, [Pt₁₂(CO)₂₄]²⁻ was used as precursor for the preparation of homometallic particles,[61-63] while the clusters [Pt₆(CO)₆(SnCl₂)₂(SnCl₃)₄]⁴⁻ and [Pt₆(CO)₈(SnCl₂)(SnCl₃)₂(PPh₃)₂]²⁻, having a specific Pt/Sn molar ratio of 1 and 2 respectively, were used for the preparation of bimetallic systems. The catalytic performance of the obtained catalysts was evaluated in the aqueous phase oxidation of HMF to FDCA in base-free conditions and compared with analogous systems prepared by metal salt impregnation method using the same metal loading and Pt/Sn molar ratio. All prepared catalysts have been thoroughly characterized by means of High Resolution Transmission Electron Microscopy, High Angle Annular Dark Field imaging (HRTEM/HAADF), Temperature Programmed Reduction (TPR), X-ray Fluorescence (XRF), X-ray Photoelectron Spectroscopy (XPS), CO chemisorption and Fourier Transform InfraRed Spectroscopy (FTIR) techniques investigating in detail their structure-property relationships.

2 Experimental

2.1 Catalyst preparation

The metal carbonyl clusters employed in this work have been prepared following the experimental procedures reported in the literature.[64, 65] For sake of completeness, some details are given below. The as-synthesized mono and bimetallic Pt-based clusters were, then, supported onto commercial titania (DT-51 Millennium Chemicals, now Tronox, pure anatase phase with surface area of 84 m²/g). Different thermal treatments were carried out on the prepared samples in order to understand the effect produced (i) in terms of structural modification and (ii) in terms of catalytic activity and stability.

2.1.1 Synthesis of [PPh4]₂[Pt₁₂(CO)₂₄] (named as Pt₁₂)

The preparation of Chini clusters is well known[62] therefore, only a brief description of the preparation method will be presented here. Na₂PtCl₆ · 6H₂O (2.00 g, 4.39 mmol) and CH₃COONa (2.00 g, 24.4 mmol) were dissolved in methanol (30 mL) and stirred under CO atmosphere (atmospheric pressure) overnight, resulting in the formation of a silky brown suspension of Na₂[Pt_{3n}(CO)_{6n}] (n \approx 30). A methanol solution of NaOH was then added dropwise in the sealed glass reactor under the presence of CO atmosphere over 1 h until a green solution of Na₂[Pt₁₂(CO)₂₄] was

formed as confirmed by IR analysis. [PPh4]2[Pt12(CO)24] was precipitated from the reaction mixture by addition of a saturated solution of [PPh4]Br in isopropanol. The solid was recovered by filtration, washed with isopropanol and extracted in acetone. A microcrystalline powder of [PPh4]2[Pt12(CO)24] (Figure S1) was eventually obtained after removal of the solvent under reduced pressure from the acetone solution.

2.1.2 Synthesis of [PPh₄]₄[Pt₆(CO)₆(SnCl₂)₂(SnCl₃)₄] (Pt/Sn molar ratio 1, labeled as Pt₁Sn₁)

SnCl₂·2H₂O (0.371 g, 1.64 mmol) and [PPh₄]Cl (0.413 g, 1.10 mmol) were added as solids to a solution of [PPh4]2[Pt12(CO)24] (1.00 g, 0.138 mmol) in acetone (30 mL). The solution turned from green to brown and it was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue washed with water (40 mL), iso-propanol (40 mL) and acetone (20 mL), and the green CH₃CN (20)mL). Α microcrystalline product extracted in powder of [PPh4]4[Pt6(CO)6(SnCl₂)2(SnCl₃)4] (Figure S2) was eventually obtained after removal of the solvent under reduced pressure from the CH₃CN solution.

2.1.3 Synthesis of $[PPh_4]_2[Pt_6(CO)_8(SnCl_2)(SnCl_3)_2(PPh_3)_2]$ (Pt/Sn molar ratio 2, labeled as Pt_2Sn_1)

PPh₃ (0.084 0.321 mmol) was added solid solution of as а to а g, [PPh4]4[Pt6(CO)6(SnCl2)2(SnCl3)4] (0.520 g, 0.161 mmol) in CH3CN (20 mL) and the mixture was stirred at room temperature under CO atmosphere for 2 h. Then, iso-propanol (80 mL) was added under CO atmosphere up to complete precipitation of a dark-brown solid, which was recovered by filtration, washed with iso-propanol (40 mL) and extracted with CH₃CN (20 mL) under CO atmosphere. A microcrystalline powder of [PPh4]2[Pt6(CO)8(SnCl2)(SnCl3)2(PPh3)2] was eventually obtained (Figure S3) by addition of iso-propanol (80 mL) to the CH₃CN solution under CO atmosphere, recovered by filtration and dried under reduced pressure.

2.1.4 Preparation of supported catalysts

The prepared carbonyl clusters have been supported on TiO₂ (2 wt. % total metal loading, *i.e.* Pt and Sn, with respect to titania, as confirmed by XRF analyses) by incipient wetness impregnation. The clusters were dissolved in CH₃CN and the solutions were slowly added to the TiO₂ support under nitrogen and stirred for 2h. Then, the solvent was removed in vacuo and the resulting powder was dried at 120°C for 2h using an oven. Some selected samples have been also thermally treated up to 450° C for 2 hours (2°C/min) in controlled atmosphere (air or H₂, 50 ml/min).

The samples prepared via cluster impregnation on TiO₂ are listed in Table 1:

The catalysts prepared using metal salt impregnation have been synthesized by incipient wetness impregnation of TiO₂ using Pt and Sn precursor solutions (H₂PtCl₆ and SnCl₂, respectively). The concentration of metal ions has been calculated in order to obtain materials having the same Pt/Sn molar ratio and metal loading as the supported cluster materials. The metal salt impregnated solids were dried at 120°C in air and thermally treated at 450°C in flowing H₂ as reported for the supported cluster materials. The list of metal catalysts prepared by salt impregnation is reported in Table 2.

2.2 Catalyst characterisation

HRTEM analyses were performed with a TEM/STEM FEI TECNAI F20 instrument, using a high-angle annular dark field imaging mode at 200 kV and with an EDS PV9761N SUTW energy dispersive X-ray spectrometer for X-ray microanalysis. The analyses of suspension were performed by diluting them in water and then the obtained suspensions were dispersed on a holey carbon film. Calculation of mean particle size was carried out using over 300 nanoparticles.

TPR (Temperature Programmed Reduction) experiments were performed using a Micromeritics ChemSorb2750 equipped with a TCD to evaluate H₂ consumption. All the tests were carried out by pretreating the samples for 30 minutes at 450°C under He flow (heating ramp 10° C/min, gas flow rate 30 mL/min). Then the samples were cooled down to 25°C, the gas flow was switched to H₂ (5% in He v/v), and the temperature was increased to 650°C (heating ramp 10° C/min, gas flow rate 30 mL/min) for the analysis.

FTIR spectra were recorded with a Perkin-Elmer Spectrum One interferometer using CaF₂ cells.

XPS spectra were recorded on a Perkin Elmer Φ 5600ci spectrometer, using a non-monochromatized AlK α excitation source (1486.6 eV). Charging effects were corrected by assigning to the C1s line of adventitious carbon a binding energy (BE) value of 284.8 eV. Atomic compositions were evaluated using sensitivity factors provided by Φ V5.4A software. Peak fitting was performed by a least-squares procedure, using Gaussian-Lorentzian peak shapes.

CO chemisorption tests were performed using a Micromeritics AutoChemII instrument. In a typical experiment, the materials were pretreated under H₂/Ar flow (50mL/min, H₂ concentration 5%) from room temperature to 200°C (temperature ramp 2°C/min, isotherm 2h). After cooling to room temperature, gas was switched to He (50mL/min) and the sample was heated up to 120°C (temperature ramp 2°C/min, isotherm 2h) to remove the hydrogen species eventually adsorbed on the

sample. Then, after cooling the sample to room temperature, 20 pulses of CO/He ($3.61*10^{-6}$ moles each) were send to the sample.

2.3 Catalytic test

The oxidation of HMF was carried out using an autoclave reactor of 100 mL capacity, equipped with a mechanical stirrer and measurement tools for temperature and pressure. The reactor was charged with an aqueous solution (25 mL distilled water) containing the appropriate amount of 5-(hydroxymethyl)furfural (99.999%, AvaBiochem) and catalyst (HMF/total metal molar ratio = 50). The autoclave was purged 3 times with O_2 (5 bar) and then pressurized at the desired pressure (10 bar). If not indicated otherwise, the temperature was increased to 110°C and the reaction mixture was stirred at 400 rpm for the indicated reaction time (0.5-3 h). Initial time (time zero) for the reaction was taken when the set point temperature was reached. At the end of the reaction, the reactor was cooled down to room temperature and the aqueous solution was centrifuged and then filtered. Then, the reaction mixture was diluted 5 or 10 times before analysis with an Agilent Infinity 1260 liquid chromatograph (HPLC-DAD) equipped with an Aminex HPX 87-H 300 mm 7.8 mm column using a 0.005 M H₂SO₄ solution as the mobile phase. An external calibration method was used for the identification, quantification of reactants and products using reference commercial samples. Particular care was devoted to the determination of the C balance, which was found to always fall between 95 and 105% (calculated as the comparison between converted HMF and the sum of the product yields).

3 Results and discussion

3.1 Preparation and characterization of the supported catalysts

Study of the cluster impregnation by means of FTIR technique

Three different cluster precursors have been employed for the preparation of the catalysts, that is $[PPh_4]_2[Pt_{12}(CO)_{24}]$ (labeled as Pt_{12}), $[PPh_4]_4[Pt_6(CO)_6(SnCl_2)_2(SnCl_3)_4]$ (Pt/Sn molar ratio 1, labeled as Pt_1Sn_1) and $[PPh_4]_2[Pt_6(CO)_8(SnCl_2)(SnCl_3)_2(PPh_3)_2]$ (Pt/Sn molar ratio 2, labeled as Pt_2Sn_1). The impregnation procedure of the synthesized clusters has been studied by means of FTIR technique using the vco bands of the different clusters as probes in order to detect the occurrence of any reactions during catalyst preparation. Particular focus has been given to the three crucial phases of such procedure, namely, in solution before impregnation, during impregnation (*i.e.* when a suspension of TiO₂ and cluster solution is present) and after solvent removal. Indeed, the interest of using molecular cluster precursors for catalyst preparation relies on the possibility to carefully control and tune the nanoparticle size, structure and (in the case of bimetallic systems) the composition of the final

nanostructured active materials. In order to achieve these goals, the intimate molecular nature of the precursor should be, in theory, retained up to thermal treatment step. Thus, the occurrence of any (uncontrolled) reaction prior to thermal decomposition of the precursor might be detrimental and therefore should be investigated.

The spectrum recorded for the **Pt**₁₂ cluster solution (black line, Figure 1a) shows the carbonyl signals of the [PPh4]₂[Pt₁₂(CO)₂₄] cluster (2047cm⁻¹ for the terminal carbonyls, 1897, 1881, 1865 and 1833cm⁻¹ for the bridging ones). After the addition of TiO₂, the spectrum of the resulting suspension (red line in Figure 1a) remained almost unchanged, suggesting that no reaction occurred at this stage. Conversely, after removal of the solvent under reduced pressure, the spectrum of the cluster impregnated powder (green line in Figure 1a) showed vco band shifted to higher wavenumbers in agreement with the formation of [Pt₁₈(CO)₃₆]²⁻. This might be due to cluster oxidation as a consequence of the intimate contact between the cluster and TiO₂. It must be remarked that the (reversible) chemical oxidation of [Pt₁₂(CO)₂₄]²⁻ to afford [Pt₁₅(CO)₃₀]²⁻ and [Pt₁₈(CO)₃₆]²⁻ is a well-known process.[61, 63, 66]

As far as the Pt_1Sn_1 cluster impregnation procedure is concerned, this cluster displays in solution a unique v_{CO} band at 2037 cm⁻¹ due to its terminal CO ligands (black line, Figure 1b). After the addition of TiO₂, this v_{CO} band remains the major one, even if a shoulder at 2010 cm⁻¹ appears (red line, Figure 1b). This suggests that Pt_1Sn_1 is still the main species present in the suspension, accompanied by a minor amount of an unknown side product. This situation remains identical after removal of the solvent in vacuo, as indicated by the fact that the IR spectrum of the cluster impregnated powder (green line, Figure 1b) shows almost the same IR pattern, apart from some broadening due to the solid state nature of the latter sample.

The carbonyl cluster Pt_2Sn_1 dissolved in acetonitrile (black line in Figure 1c) showed the expected vco bands due to terminal (2043 and 2028 cm⁻¹) and edge bridging CO ligands (1882 and 1831 cm⁻¹). The presence of a shoulder at 2012 cm⁻¹ could indicate the formation of traces of [Pt₆(CO)₆(SnCl₂)₂(SnCl₃)₂(PPh₃)₂]²⁻, due to partial decarbonylation of Pt_2Sn_1 under nitrogen atmosphere. Indeed, Pt_2Sn_1 is stable under CO atmosphere, whereas under nitrogen atmosphere slowly loses CO resulting in the formation of [Pt₆(CO)₆(SnCl₂)₂(SnCl₃)₂(PPh₃)₂]²⁻. This is not a problem, since the two clusters have the same Pt/Sn composition. Taking into account the aforementioned results, the described impregnation steps did not lead to significant changes in the vco bands, indicating that Pt_2Sn_1 did not undergo any structural modification during the impregnation procedure. Moreover, XRF analyses on all supported catalysts (Table 1) indicate that the real metal content is equal to the nominal one based on the amount of cluster deposited on support.

FTIR analyses have been conducted also during the thermal treatment of the supported Pt_1Sn_1 material. Cluster decomposition begins after drying in oven at 120°C for 2 h, since the v_{CO} bands of the spectra recorded before (green line in Figure 1d) and after such treatment (grey line in Figure 1d) are completely different. Then, complete cluster decomposition occurs after the thermal treatment at 450°C, irrespective of the atmosphere used, as indicated by the disappearance of all the v_{CO} bands in both 2-Pt₁Sn₁-H₂ and 2-Pt₁Sn₁-O₂ samples (yellow and orange lines, Figure 1d).

Effect of thermal treatment on Pt/Sn supported materials

FTIR analyses demonstrated that complete cluster decomposition occurs after thermal treatment at 450°C, irrespective of the atmosphere used. Since, the interest of using molecular cluster precursors for catalyst preparation relies on the possibility to carefully control and tune nanoparticle size, structure and composition, the effect of thermal treatment of 2-Pt₁Sn₁ dried sample in different atmosphere was studied. In particular, dried sample was treated at 450°C in flowing air or H₂ and the obtained materials were characterized thoroughly by means of BET, HRTEM/STEM, EDX, H₂-TPR and XPS (Table 3).

BET surface area results obtained for all catalysts point out that Pt/Sn cluster deposition has a little influence on the textural properties of bare titania (surface area 84 m²/g). Nevertheless, the dried sample show a significant surface area decrease, indicating that cluster residues can partially block the pores of the support. On the contrary, catalyst treatments with H₂ or air, lead to surface area values similar to the bare support, indicating that the complete cluster decomposition frees the porosity, being this effect more evident in the presence of air.

HRTEM/STEM analysis was used to obtain information on the morphology in terms of mean particle size, particle size distribution and composition of the metallic species after the treatment at 450° C both in air (2-Pt₁Sn₁-O₂ – Figure 2a) and H₂ atmosphere (2-Pt₁Sn₁-H₂ Figure 2b). Representative HRTEM images and particle size distribution histogram for the dried sample are reported in Figure S4. For this material, the analysis shows a mean particle size of 1.2 nm, with narrow particle size distribution and with relatively good dispersion of PtSn nanoparticles onto TiO₂.

Figures 2 shows that, the treatment at 450°C, both in air and H2, caused a small increase of nanoparticles dimension and the average diameter was only slightly influenced by the adopted thermal treatment atmosphere (2.1 nm in H₂ versus 2.6 nm in Air). However, the skewness of the Gaussian distribution significantly changed depending on the used atmosphere. Indeed, when hydrogen was used, the distribution shifted towards smaller particle diameter and narrower particle size distribution; moreover, in air treated sample some large nanoparticles were observed.

On the other hand, EDX analyses and mapping evidenced that the distribution of the two metals over support surface is strongly affected by the used atmosphere. In fact, in the H₂-treated sample, high concentrations of Pt and Sn are detected in the same area of the support surface (Figure 3a) while in the air-treated sample Sn seems to be evenly spread on the TiO₂ surface and Pt is mainly present as segregated nanoparticles (Figure 3b). This feature suggests that reducing atmosphere prevents the well-known out-diffusion of Sn from the cluster structure[67, 68] and bimetallic Pt/Sn nanoparticles could be obtained in such reducing conditions.

XRD patterns obtained over 2-Pt₁Sn₁ samples did not allow to identify the presence of Pt/Sn species formed on the different catalysts due to the very low amount of metals and their small crystallite size, below 5 nm. Nevertheless, the X-ray diffraction pattern of a similar sample prepared with a total metal loading of 4% w/w, reported in Figure S5, confirmed the presence of the PtSn alloy (reflexes at $2\theta = 30$, 42, 44, reference code 00-008-0192) in the sample treated in H2 at 450°C. This specie was not evident in the sample treated in air.

In order to gain further information on the surface features of the thermally treated Pt₁Sn₁based materials, XPS analysis has been performed and compared with the dried Pt₁Sn₁ material. The most relevant results, summarized in Table 3, (see also Figures S6 and S7 and Table S1), showed that the surface Pt/Sn molar ratios were appreciably lower than the corresponding bulk values (close to 1 for all the three samples, as revealed by XRF analyses, see Table 1). This difference could be due to a possible surface segregation of Sn that results in an enrichment of this element with respect to Pt, as far as the XPS sampling depth is concerned.[69] It could be hypothesized that the driving force for Sn out-diffusion might be its higher tendency to oxidation compared to Pt, in agreement with previous works on similar Pt-Sn systems. [49, 70] In fact, analysis of the Sn3d peak revealed two bands arising from spin-orbit splitting phenomena, located at 486.7 eV (Sn3d_{5/2}) and 495.1 eV (Sn3d_{3/2}) irrespective of the considered sample (see also Figure S6). Such BE values indicate the absence of Sn(0) and Sn-Pt metallic alloys in appreciable amounts, and are compatible with Sn(II) and/or Sn(IV) oxidized species.[71-74] At variance from Sn, the Pt oxidation state was affected by the thermal treatment atmosphere. A careful analysis of the Pt4f peak revealed indeed the co-presence of Pt(0), Pt(II), and Pt(IV) species for all specimens[72-74] but a Pt(0)/[Pt(II)+Pt(IV)] content much higher for sample 2-Pt₁Sn₁-H₂ than for the other two systems. Overall, XPS data indicate that during the drying procedure the majority of the Pt is oxidized from its original oxidation state (*i.e.* metallic Pt), a situation that is not appreciably changed by the thermal treatment in air. Conversely, the use of a reducing atmosphere partially restores the oxidation state of Pt, yielding a Pt(0)/[Pt(II)+Pt(IV)] value of 0.95. Interestingly, the latter effect is also paralleled by the highest Pt/Sn molar ratio (Table 3). In other words, the use

of a reducing atmosphere also promotes an enhanced Pt/Sn intermixing, a phenomenon already evidenced by EDX data.

The above considerations on Pt and Sn oxidation states for **2-Pt₁Sn₁-H₂**, **2-Pt₁Sn₁-O₂** and **2-Pt₁Sn₁** samples have been further investigated and confirmed by TPR analyses. In fact, the former two samples revealed a very similar TPR behavior, characterized by two main peaks at 170 and 360°C (Figure 4), indicating once again that the oxidation state of the metals does not substantially change after an increase of the temperature treatment in the same oxidizing atmosphere. The first of the two peaks could be attributed to the reduction of Pt-O-Sn species, where Pt(II)/Pt(IV) and Sn(IV) are reduced to Pt(0) and Sn(II), respectively, while the second could be due to the subsequent Sn(II) reduction to Sn(0).[75] Such peculiar behavior revealed that the use of bimetallic cluster as precursor leads to an interaction between the two metals from the initial catalyst synthesis step which is an essential parameter for achieving the synthesis of bimetallic random alloyed nanoparticles. On the contrary, the reducing atmosphere leads to an almost complete reduction of the metal species, as could be seen from the **2-Pt₁Sn₁-H₂** profile. The presence of the peak at 175°C underlines that some oxidized species are still present after the reduction process, as already revealed by XPS analysis. The presence of some Sn(IV) even after the reducing treatment could be caused by the tendency of this metal to stay in the oxidized form.

Effect of Pt/Sn ratio on supported materials

The effect of metal composition was studied preparing and characterizing a monometallic catalyst (2-Pt-H₂) and a bimetallic material with different Pt/Sn ratio ($2-Pt_2Sn_1-H_2$). For comparison, catalysts with the same metal molar ratio of the cluster-based materials were prepared by incipient wetness impregnation of the metal salts (Table 4). Moreover, Pt dispersion is presented in Table 4 for selected samples.

TEM/STEM and EDX analyses were carried out and compared to the previously reported samples to verify the effect of Pt/Sn molar ratio on the dispersion of active phase over the support after high temperature (450° C) treatment under H₂.

A strong effect of Sn content on the final formation of the metal nanoparticle size in the three samples was found comparing the average nanoparticle size for 2-Pt-H₂, 2-Pt₂Sn₁-H₂ and 2-Pt₁Sn₁-H₂ (Table 4; Figure 5a and 5b). Sn introduction seems to decrease the mean metal particle size only at low content, with sample 2-Pt₂Sn₁-H₂. On the other hand, 2-Pt₁Sn₁-H₂ showed the same mean particle size as the monometallic material (2-Pt-H₂). It is worth noting that, even if the mean particle size of those two samples (i.e. 2-Pt₁Sn₁-H₂ and 2-Pt-H₂) is at similar range, the measured Pt dispersion of

the bimetallic sample is lower than the monometallic one (12.7 and 20.5%, respectively), probably due to Sn-enrichment of the Pt nanoparticle surface, as detected by XPS. The aforementioned observations indicate that the preparation of Pt/Sn bimetallic nanoparticles from carbonyl cluster precursors is influenced by Sn content, and the right amount of Sn to obtain smaller mean particle size and controlled Pt surface exposure could be therefore optimized.

In addition to this, EDX mapping for the $2-Pt_2Sn_1-H_2$ sample showed that Sn is dispersed over the support surface, while Pt is mainly present as segregated nanoparticles (Figure 5c). This feature is in contrast with what previously reported for the $2-Pt_1Sn_1-H_2$, since in the latter, Pt/Sn close proximity were observed, (Figure 2). Therefore, even if the lower amount of Sn lead to the formation of smaller nanoparticles, their composition could not be considered as stable since it segregated during the reductive thermal treatment.

For comparison, catalysts with the same metal molar ratio of the cluster-based materials were prepared by incipient wetness impregnation of the metal salts. TEM/STEM analyses have been performed on samples thermal treated in H₂, with the aim to understand if the different synthetic protocols have a significant effect on the structural features of the synthesized materials. TEM analysis of the **2-Pt-s-H₂** sample showed a poor Pt dispersion over the support surface (Figure S8). Indeed, Pt is present as 4-5 nm nanoparticles and with some large Pt aggregates. On the contrary, TEM/STEM analysis of the **2-Pt₁Sn₁-s-H₂** sample showed that the co-impregnation of the two metals led to an improved NPs dispersion, confirming that the presence of Sn favors the formation smaller nanoparticles also in the case of the incipient wetness impregnation (Figure S9). Moreover, EDX analysis performed on this sample confirmed that, in contrast to **2-Pt₁Sn₁-H₂** cluster derived sample, Sn tend to disperse rather than react with Pt nanoparticles (Figure 6b). Taking everything into account, it is possible to state that metal salt impregnation protocol cannot ensure the same metal particle size control and surface metal distribution obtained via controlled metal cluster decomposition.

3.2 Catalytic tests

The catalytic performance of all prepared materials was tested in the aqueous phase oxidation of HMF to FDCA in base-free conditions. The general reaction pathway for HMF oxidation is presented in **Scheme 1**. The first oxidation reaction can either involve the aldehyde group producing 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) or the alcoholic group. In the latter case, the formation of 2,5-diformylfuran (DFF) occurs but it is mainly observed in the absence of an added base and with metals other than Au.[76-78] Then, a second oxidation step takes place and 5-formyl-2-furancaboxylic acid (FFCA) is obtained. Consecutive oxidation of this molecule leads to the

formation of 2,5-furandicarboxylic acid (FDCA). These molecules were the only detected products in this study.

3.2.1 Preliminary screening

At first, reference catalysts prepared using metal salts impregnation, were tested for HMF oxidation. Figure S10 depicts the catalytic activity and product distribution over the monometallic **2**-**Pt-s-H**₂ and **2-Sn-s-H**₂. Such preliminary tests revealed that among the two metals, just Pt is active toward HMF oxidation in base-free conditions in agreement with previous reports. In detail, Pt is able to convert HMF into HMFCA and DFF, being the latter more abundant than the former (2 and 18%, respectively). However, HMF conversion and product yields were very low.

This result is in good agreement with the literature, since, under base-free conditions, DFF formation is known to be favored over HMFCA, especially using Pt based catalysts. Both products of consecutive oxidation, i.e. FFCA and FDCA were detected, and carbon balance was always higher than 95%.

Superior results in terms of HMF conversion and target product (FDCA) yield were obtained by using the materials prepared via cluster impregnation, indicating that such synthetic strategy has a positive effect in determining and improving the catalytic properties of the material. This feature could be ascribed to the higher dispersion and smaller mean metal particle size of the cluster derived material (**2-Pt-H**₂) with respect to its metal salt impregnated counterpart (**2-Pt-s-H**₂).

3.2.2 Sn content effect on the catalytic activity

Comparison of catalytic performance of monometallic Pt and bimetallic Pt-Sn catalysts via the metal cluster decomposition route is presented in Figure 7.

The catalytic results show that a Pt/Sn molar ratio equivalent to 2 (as in $2-Pt_2Sn_1-H_2$) seems to be detrimental for both HMF conversion and FDCA yield, while the equimolar catalyst provides higher FDCA yield if compared to the monometallic catalyst (13 and 9% for $2-Pt_1Sn_1-H_2$ and $2-Pt-H_2$, respectively). This result is of particular interest taking into account that Pt, which has been proven to be the active metal, is more diluted in $2-Pt_1Sn_1-H_2$ than in the other two samples, thus the best result in term of FDCA yield were obtained with the catalyst having the lowest active metal content (Table 5). In addition, by calculating and comparing the TON (turnover number) of the three samples it is evident that the catalytically active species formed in the $2-Pt_1Sn_1-H_2$ sample are the most active in the studied reaction, since the TON related to this sample is one of order of magnitude higher than the ones calculated for the other two samples.

The lower catalytic activity of 2-Pt₂Sn₁-H₂ could be ascribed to the higher tendency of smaller Ptenriched nanoparticles to undergo overoxidation in the presence of high oxygen pressure and/or chemical poisoning, leading thus to a less active catalyst.[79-83]

A similar catalytic behavior was displayed by the reference catalysts prepared from metal salts impregnation being the best catalyst the material obtained with the equimolar loading of the two metals. On the contrary, the sample having Pt/Sn molar ratio equal to 2 led to poor catalytic performance (Figure S11). Furthermore, comparing the results of salts derived catalysts with those obtained via cluster impregnation (Figure 8) demonstrated that better catalytic performance was always obtained using the catalyst prepared from carbonyl cluster decomposition. This confirmed, once again, the higher potential of cluster impregnated catalysts than the metal salt impregnated ones.

Finally, the effect of the thermal treatment on the catalytic behavior has been studied. In Figure 9, the comparison of the catalytic results obtained using the Pt_1Sn_1 materials thermally treated under different conditions is reported.

The catalytic results showed that thermal treatment plays a key role in terms of catalyst activity and yield. Indeed, reducing atmosphere leads to higher catalytic performances if compared to those obtained by using dried and calcined catalysts, indicating that not only the appropriate Pt/Sn ratio is required to obtain active catalysts, but also control of Pt oxidation state (metallic versus oxidized Pt species) and/or Pt/Sn aggregation play a key role in determining catalyst activity. Based on the aforementioned catalytic and characterization data, it is evident that the presence of Sn with a specific metal molar ratio of 1/1 has a significant influence and improvement in terms of activity. Moreover, in terms of mean particle size, the presence of Sn in bimetallic Pt/Sn supported nanoparticles, via the metal impregnation decomposition route and heat treatment under H₂ forms small nanoparticles with mean metal particle size of 2 nm and narrow particle size distribution.

In conclusion, by comparing the catalytic results showed by the most performing catalyst studied in this work (i.e. $2-Pt_1Sn_1-H_2$) with the ones reported in the literature for similar catalytic systems, it is evident that the catalytic performance in terms of activity and yield of the presented bimetallic system is at similar level with comparable catalytic systems operating at similar operative conditions.[8, 23, 24] On the other hand, if the same comparison is made by taking into account as well Pt-based systems operating under basic conditions, the $2-Pt_1Sn_1-H_2$ system is outperformed by other catalytic systems, such as Pt-Bi/TiO₂, Pt/ZrO₂ [26] or platinum nanoparticles on a cerium coordination polymer.[25]

3.2.3 Catalyst stability and reproducibility

To determine long-term catalytic performance, the catalyst stability has been studied, by reusing the spent catalysts in the case of 2-Pt-H₂ and 2-Pt₁Sn₁-H₂ under the same operative conditions. Such tests demonstrated that 2-Pt-H₂ catalyst suffers from significant deactivation, since HMF conversion dramatically dropped from 63 to 24% after just one cycle, (Figure 10).

On the other hand, the $2-Pt_1Sn_1-H_2$ showed higher stability, since the catalyst second cycle guaranteed the same HMF conversion and products yield respect to first use (Figure 11). The third cycle of this catalyst showed lower conversion (49%) and lower FDCA yield (11%); nevertheless, these values still remained higher than the monometallic counterpart.

In order to understand the reasons of the different deactivation trends of the two materials, TEM analyses have been performed over the two used catalysts and mean metal particle size and metal particle size distribution have been evaluated. Comparison of the mean metal nanoparticle size before and after the reaction, shows that Pt nanoparticles in **2-Pt-H**₂ catalyst suffered from sintering during the reaction, since mean Pt particle size increased from to 2.0 to 5.5 nm. In addition, some nanoparticles having diameter higher than 10 nm were detected (Figure S12). On the other hand, **2-Pt₁Sn₁-H**₂ did not undergo significant sintering, since mean metal particle size did not vary significantly (Figure S13). Moreover, it seems that the Pt/Sn nanoparticles did not undergo any change in chemical composition, since the EDX maps on the used catalyst showed that the two metals are still present and in close proximity even after the reaction, as detected in the fresh sample (Figure S12). Chemical analysis of the filtrate indicated that the amount of platinum and tin leached out at the end of the reaction cycles was less than 1% of the original nominal loading confirming the high relative stability of this catalyst formulation.

To better elucidate deactivation process, XPS analysis has been performed on the used catalyst (Table S1). The analysis revealed that the Pt(0) species content drops from 49% in the fresh catalyst to 36% (*i.e.* by a factor of 0.73) after recycling tests in agreement with the decrease by a factor of 0.72 of HMF conversion (from 68 to 49%) after 3 uses. Moreover, comparing these results with the ones obtained for the series of Pt₁Sn₁-based catalysts (dried and heat treatment under air or H₂) it is evident that the concentration of Pt(0) species is strongly correlated to the catalyst ability to convert HMF, since HMF conversion was found to be linearly correlated with the presence of metallic Pt species (Fig. 12). In light of all these observations, it has been hypothesized that Sn enhances structural nanoparticle stability, which is responsible for the higher **2-Pt₁Sn₁-H₂** catalytic stability (maintaining

mean particle size and to a lesser extent Pt oxidation state), and high Pt(0) concentration is fundamental to achieve and maintain high catalyst activity.

In addition to the aforementioned points and with the aim to validate the reproducibility of the synthetic protocol, two additional batches of the $2-Pt_1Sn_1-H_2$ were prepared and tested. These two additional tests showed that the experimental procedure employed for the synthesis of the catalyst can afford a good level of catalyst reproducibility in both terms of catalytic performances and carbon balance, being the latter >99% (see Figure S15).

4 Conclusions

The present work demonstrated the possibility to develop Pt-based active and stable catalysts able to oxidize HMF in base-free aqueous conditions. The synthesis of TiO₂-supported Pt and Pt/Sn nanoparticles from carbonyl cluster decomposition with a controlled structure shows the crucial role played by the synthetic strategy in the preparation of active and stable Pt-based supported catalysts and this preparation method has not reported previously for the specific reaction. In particular, the use of carbonyl clusters as precursors for the synthesis led to the formation of metal particles having well controlled dimension and relatively narrow particle size distribution, whose catalytic performances were significant higher respect to the ones obtained by their counterparts prepared via metal salt impregnation. Moreover, the addition of Sn to Pt in an equimolar amount was demonstrated to lead to the formation of unique active sites with significant improved stability in the base-free oxidation of HMF. Finally, the influence of heat treatment and usage of H₂ showed to be beneficial for the synthesis of active supported bimetallic Pt/Sn nanoparticles. In the future, we will focus on the optimization of the preparation method (i.e. by investigating more sustainable solvent for cluster production and/or choosing less expensive active metals) and experimental conditions to improve the yield towards FDCA and overall process sustainability.

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Figures

Figure 1. FTIR spectra recorded during the Pt_{12} (a), Pt_1Sn_1 (b), Pt_2Sn_1 (c) impregnation protocol and recorded on 2- Pt_1Sn_1 derived-materials thermally treated under different conditions (d).

Figure 2. HR-TEM images and particle size distribution histograms of the $2-Pt_1Sn_1$ catalyst treated in air (a) and H₂ (b) at 450°C.

Figure 3. STEM image along with the corresponding Pt-M α , Sn-L α and (Pt-M & Sn-L) elemental maps from the same area regarding 2-Pt₁Sn₁ catalyst treated in H₂ (a) and air (b). (For interpretation of the reference to colour in this figure, the reader is referred to the Web version of the article).

Figure 4. H₂-TPR profiles of 2-Pt₁Sn₁ sample thermally treated in different conditions. (a) dried sample, (b) treated at 450°C in air, (c) treated at 450°C in H₂.

Figure 5. TEM images and particle size distribution histograms of the 2-Pt-H₂ (a) and Pt₂Sn₁-H₂ (b) samples; STEM image along with the corresponding Pt-L α , Sn-K α and (Pt-L & Sn-K) elemental maps from the same area regarding 2-Pt₁Sn₁ catalyst (c).

Figure 6. Comparison of Pt samples prepared by salts or cluster impregnation. Operative conditions: temperature 110°C, time 4 h, O₂ pressure 10bar, molar ratio HMF/total metal=50.

Figure 7. Catalytic performances of cluster impregnated catalysts. Operative conditions: temperature 110°C, O₂ pressure 10bar, molar ratio HMF/total metal=50.

Figure 8. HMF Conversion and FDCA yield according the catalyst Sn/Pt molar ratio (solid line cluster impregnated catalysts, dashed line metal salt impregnated catalysts). Operative conditions: temperature 110°C, time 4 h, O₂ pressure 10bar, molar ratio HMF/total metal=50.

Figure 9. Effect of the thermal treatment on the catalysts prepared via Pt₁Sn₁ impregnation. Operative conditions: temperature 110°C, time 4 h, O₂ pressure 10bar, molar ratio HMF/total metal=50.

Figure 10. 2-Pt-H₂ reuse tests. Operative conditions: temperature 110°C, O₂ pressure 10bar, molar ratio HMF/total metal=50.

Figure 11. 2-Pt₁Sn₁-H₂ reuse tests. Operative conditions: temperature 110°C, time 4 h, O₂ pressure 10bar, molar ratio HMF/total metal=50.

Figure 12. Correlation between HMF conversion and Pt(0) content revealed by XPS analyses of the Pt1Sn1-derived samples



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Figure 12. Correlation between HMF conversion and Pt(0) content revealed by XPS analyses.





Table

Sample	Metal (Pt+Sn) loading (w/w %)	Cluster Precursor	Nominal Pt/Sn molar ratio	Experimental Pt/Sn molar ratio (XRF)	Thermal treatment
2-Pt-H ₂	2	Pt12	-	-	Air 120°C H ₂ 450°C
2-Pt ₂ Sn ₁ - H ₂	2	Pt ₂ Sn ₁	2	1.95	Air 120°C H ₂ 450°C
2-Pt ₁ Sn ₁	2	Pt_1Sn_1	1	1.01	Air 120°C
2-Pt ₁ Sn ₁ - H ₂	2	Pt ₁ Sn ₁	1	1.00	Air 120°C H ₂ 450°C
2-Pt ₁ Sn ₁ - O ₂	2	Pt ₁ Sn ₁	1	1.03	Air 120°C Air 450°C

Table 1. Sample name, metal loading and thermal treatment of the cluster derived materials.

Sample	Metal (Pt+Sn) loading (w/w %)	Salt Precursor	Nominal Pt/Sn molar ratio	Thermal treatment
2-Pt-s-H ₂	2	H ₂ PtCl ₆	-	Air 120°C H2 450°C
2-Pt ₂ Sn ₁ -s-H ₂	2	H2PtCl6 SnCl2	2	Air 120°C H ₂ 450°C
2-Pt ₁ Sn ₁ -s-H ₂	2	H2PtCl6 SnCl2	1	Air 120°C H2 450°C
2-Sn-s-H ₂	2	SnCl ₂	0	Air 120°C H2 450°C

Table 2. Sample name, metal loading and thermal treatment of the metal salt-impregnated catalysts.

Sample	Thermal treatment	Surface Area (m²/g)	Metal Avg. Diameter (nm)	Surface Pt/Sn molar ratio	Pt(0)/[Pt(II)+Pt(IV)] molar ratio
2-Pt ₁ Sn ₁	Dried	66	1.2±0.5	0.30	0.10
2-Pt ₁ Sn ₁ -O ₂	Air 450°C	84	2.6±1.6	0.40	0.10
$2-Pt_1Sn_1-H_2$	H ₂ 450°C	73	2.1±1.0	0.45	0.95

Table 3. Characterization of the Pt_1Sn_1 cluster derived materials treated at different temperature. Surface area (from BET analyses), mean diameter of metal nanoparticles (from TEM) and Pt/Sn and Pt(0)/[Pt(II)+Pt(IV)] molar ratio (from XPS).

Samula	Metal	Metal	Pt Dispersion (%)
Sample	precursors	Avg. Diameter (nm)	
2-Pt ₁ Sn ₁ -H ₂		2.1±1.0	12.7
2-Pt ₂ Sn ₁ -H ₂	Cluster	1.2±0.4	23
2-Pt-H ₂		2.0±1.0	20.5
2-Pt-s-H ₂		4-5 + agglomerates	-
$2-Pt_2Sn_1-s-H_2$	Salts	-	-
2-Pt ₁ Sn ₁ -s-H ₂		2.4±9.5	-

Table 4. Characterization of the supported catalysts with different Pt/Sn molar ration synthesized using cluster and metal salt precursors.

Catalyst	HMF/Pt molar ratio	FDCA yield (%)	TON (FDCA produced/Pt exposed)
2-Pt-H ₂	50	9	22
2-Pt ₂ Sn ₁ -H ₂	75	5	16
2-Pt ₁ Sn ₁ -H ₂	100	13	102

Table 5. Comparison of FDCA yield and TON (calculated as mol of FDCA produced/mol of Pt exposed) according to the Pt weight content in the samples prepared via metal cluster decomposition.