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Dip-coating on TiO_2 foams using a suspension of Pt–TiO_2 nanopowder synthesized by laser pyrolysis—preliminary evaluation of the catalytic performances of the resulting composites in deVOC reactions

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Abstract

As an extension of a study to generate ceramic-metal nanosized composites further deposited on ceramic foams, here we describe a new route to prepare Pt–TiO_2 nanopowders of controlled metallic size and their further coating of TiO_2 foams. Their efficiency as catalysts in volatile organic compound elimination (deVOC) reactions was evaluated and compared to those of the corresponding classical unsupported mixed powders.

Composite metal/ceramic nanopowders (Pt–TiO_2) were synthesized by laser pyrolysis using organo-metallic precursors. Successive dip-coatings on TiO_2 foams with aqueous slurries of nanodispersed Pt–TiO_2 particles were then achieved. Both foam-supported and unsupported Pt–TiO_2 grains of about 20 nm could be stabilized, confirming no significant particles coalescence after a thermal treatment at 460 °C. Both proved equally efficient catalysts for the total oxidation of methanol, selected as probe deVOC reaction, thereby demonstrating that the dispersion of the nanopowders over the preformed ceramics does not modify their catalytic performances.

Keywords: Laser pyrolysis; Composites

1. Introduction

Among the huge range of applications of nanostructured materials, catalysis and in particular environmental catalysis i.e. new processes for green chemistry, is a privileged domain of applications. In this field, the emission of volatile organic compounds (VOC) is an important environmental problem and more efficient processes and catalysts are needed to eliminate such products from various effluents. Due to the high surface of the nanostructured materials, good catalytic properties can be expected. Indeed, a high dispersion of the active phase (oxide, metal) and its adequate retention on the support strongly increase the catalytic efficiency as well as the durability of the solids. The catalyst performance could be improved by e.g. controlling the dispersion and the stability of the active nanophases on a high surface (macroporous) supports.

Nanoparticles with well defined chemical composition, size and structure[1–3] and a high specific surface can be obtained by the laser pyrolysis method. This method is based on the interaction of a powerful IR laser beam with a mixture of gaseous or liquid precursors, one of them absorbing the laser radiation. The temperature increases rapidly, leading to the decomposition of the precursors. An incandescent flame is observed in the interaction zone where nanoparticles nucleate and grow. The residence time adjusted by the carrier gas flow allows the control of the nanoparticle size. Their chemical composition depends on the nature and the content of the different reagents in the precursor mixture.

In this paper, we present the extension of the laser pyrolysis method to the synthesis of an active composite Pt–TiO_2 for catalytic applications. Pure TiO_2 nanopowders were already obtained by laser pyrolysis from various liquid precursors such as: titanium isopropoxide (TTIP), $Ti(OC_3H_7)_4$[4,5] or titanium ethoxide $Ti(OC_2H_5)_4$.[4] Doped TiO_2 nanopowders (Mo,W,Al,Ga) were also prepared by laser pyrolysis from TTIP

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precursor.[6,7] However, to our knowledge, the synthesis of Pt doped TiO_2 by laser pyrolysis has not yet been reported.

In that paper, we present:

- a one step preparation of nanopowders of platinum well dispersed over TiO_2 (Pt–TiO_2 composite nanopowders) by laser pyrolysis;
- the further coating of such powders on a ceramic (TiO_2) foam using a simple procedure, yielding Pt–TiO_2/TiO_2 foam-composites;
- the performances of those composite materials (nanopowders and foam-composites) for catalytic methanol oxidation (deVOC).

2. Experimental

2.1. Pt–TiO_2 preparation

The Pt–TiO_2 nanopowders were synthesized by laser pyrolysis using TTIP as Ti precursor.[4,5] The solution containing the precursors was prepared using a procedure very similar to the one described by Ströbel,[8] by first dissolving appropriate amounts of platinum acetylacetonate Pt(Acac) (Aldrich, 97%) in a xylene (Aldrich, 98%)/ethylacetate (SDS, purum) mixture (65:35 vol/vol) and then mixing it with TTIP (Aldrich, 97%). Nevertheless such mixture absorbs weakly the laser radiation so ethylene C_2H_4 was added as sensitizer gas. In the experiments reported here, the aerosol droplets were carried out in an argon flow (2 l min^{-1}) into the reaction chamber through a 6 mm in diameter nozzle.

2.2. Pt–TiO_2 deposition on TiO_2 foams

TiO_2 is widely used as photocatalyst as suggested by the prolific literature on the subject.[9–18] Suspensions of TiO_2 often are aqueous.[11–14,16,17] So an aqueous suspension of Pt–TiO_2 was prepared at a concentration of 10 g/l. The powder tended to be slightly hydrophobic and had to be ground in a mortar with a small quantity of water prior the addition of all the water. It was sonicated in order to obtain a good dispersion of the nanopowder.

Ceramic foams made of TiO_2 (20 ppi) were provided by the CTI company (France), which is involved in the NACACOMO program. They were cleaned in warm water, ethanol and then dried. Multiple layers of Pt–TiO_2 have been deposited on each TiO_2 substrate. After each dip into the colloidal suspension, the samples were dried in air at room temperature, then heated at 80 °C. After 3–6 dips, a thermal treatment was carried out in air at 460 °C during 3 h. After every operation, the samples were carefully and precisely weighted.

2.3. Characterization

Chemical analyses were performed using conventional methods (CNRS analytical center/Solaize-France) with a relative uncertainty of ±2% for C, O, and of ±3% for Pt, Ti determination. Specific surface area (S_{BET}) was measured by the BET method using a Micromeritics Flowsorb 2300 instrument. Powder density (ρ) was measured by Helium pycnometry (Micromeritics AccuPyc 1330). An equivalent diameter (D) was deduced from S_{BET} and ρ, assuming spherical shape particles. The size of the grains dispersed in water was obtained from photo correlation spectroscopy (PCS) using a Malvern HS1000 apparatus. An X-ray diffraction (XRD) powder pattern was obtained with an automated diffractometer (Philips, APD1700) using the Cu Kα radiation and the crystallite size was evaluated using the well-known Scherrer equation.

The electrophoretic mobility of the suspension was studied as a function of pH. The measurements were carried out with a Delsa 440 instrument (Beckman Coulter). Aqueous dispersions of pure TiO_2 (P25 from Degussa), used as reference, and the above synthesized Pt–TiO_2 nanoparticles were prepared at a concentration of 0.2 g l^{-1}. The pH was monitored with NaOH 0.1 M and HCl 0.1 M. A salt, KCl, was used as electrolyte at concentrations of 10^{-2} and 10^{-3} M.

Microstructural analyses were performed using a TEM instrument (JEOL 2000FX, 200 kV) for the powder (after a heat treatment at 460 °C) and a FE-SEM apparatus (LEO-1530) for the deposits. The surface of Pt–TiO_2 particles as well as the Pt particle size analysis were investigated by TEM (Philips CM120 microscope, equipped with a LaB6 filament at 120 kV) coupled to an EDX analyser (fixed probe). Electron microdiffraction patterns were also recorded to identify the nature of the platinum-bearing particles. The samples were at first occluded in a resin that was cut into sections of 30–50 nm with a microtome equipped with a diamond cutter, before they were supported on a carbon-coated nickel grid.

H_2-chemisorption was performed by using a Micromeritics AutoChem 2910 instrument. The sample was first reduced under H_2 at 450 °C during 8 h, and then purged by an Ar flow for 6 h at 450 °C. H_2-chemisorption was performed using a dynamic pulse method at ambient temperature with a loop gas of 5% H_2–Ar until the integrated areas of consecutive pulses were constant.

2.4. Catalytic tests: methanol oxidation

Such studies required the use of an isothermal flow reactor able to work semi-automatically, in order to provide highly reproducible results. The method used was described elsewhere.[19]

The gaseous mixture used for the reaction consisted of oxygen and methanol vapor, diluted by helium. The methanol flow rate was managed by using a 'saturator', containing a hot (60–80 °C) methanol solution through which the O_2–He mixture was bubbling. The final composition of the feed is controlled by the methanol partial pressure by means of a condenser in which the temperature of the circulating cooling fluid was fixed by a cryostat at 11 °C. The catalytic reactor consists of a straight Pyrex glass tube where the catalyst is held by two quartz wool plugs.

A sample loop connected to a ten-port valve allows to inject into a gas chromatograph (GC) either a known volume of the gas mixture from the reactor, or the reactant feed (by-pass position). The sample loops are connected so as to inject into the GC

analyzer (involving a column packed with chromosorb 107) a known volume (0.5 ml for the FID), either of the reactant feed or of the gas mixture. A computerized system was used for the acquisition and treatment of the chromatograms. The apparatus allowed the accurate measurement of the surface area of the formaldehyde peak down to a value corresponding to a yield of 0.5%, for an initial methanol concentration of 7.7%.

3. Results and discussion

3.1. Characterization of the powder

The results of the Pt–TiO_2 nanopowder characterization (particle size and composition) are presented in Table 1. It must be noted that the Pt/Ti ratios in solution and in the resulting powder are similar. A satisfactory agreement is observed between the grain size measured by BET or PCS in suspension which indicates a good dispersion of the nanopowders. Chemical analyses show that the powder contains a small amount of free carbon, probably stemming from a partial cracking of ethylene[5] and/or the decomposition of the secondary products. It is totally eliminated after heat treatment under air at 400 °C during 3 h. The XRD pattern (not shown here) corresponds to a mixture of phases involving a major anatase phase and a small amount of rutile. During the synthesis of TiO_2 by laser pyrolysis, anatase is usually the only crystalline phase that forms although increasing percentages of rutile were observed at higher reaction temperature.[5] In a previous case, it has been suggested[20] that the formation of a rutile phase was promoted by the formation of PtO_2 whose structure is similar to that of rutile. Particle sizes range between 15 and 20 nm (TEM image, Fig. 1), which is in agreement with the calculated equivalent diameter. Very few aggregates of around 55 nm were observed. Fig. 2 shows a better resolved TEM image of Pt–TiO_2 with platinum particles

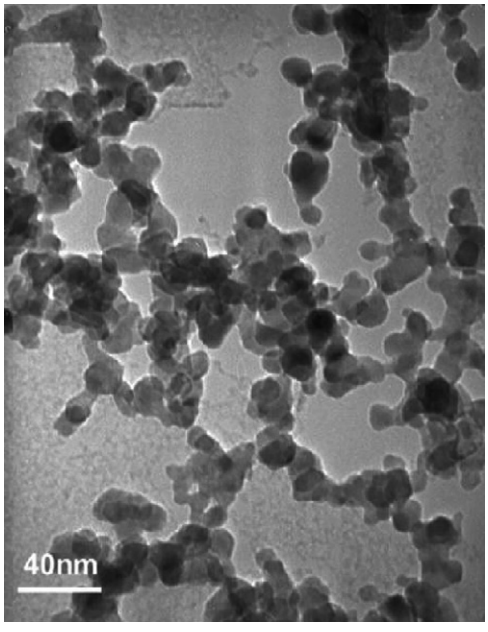

Fig. 1. TEM of the Pt–TiO_2 nanopowder after a thermal treatment at 460 °C.

Table 1
Main experimental parameters and characterization of Pt–TiO_2 nanoparticles

Powder	C_2H_4 flow ($cm^3\ min^{-1}$)	Pt/Ti ratio (wt.%) solution	Pt/Ti ratio (wt.%) powder	Pt/(Pt–TiO_2) ratio (wt.%)	S_{BET}[a] ($m^2\ g^{-1}$)	Density[a] ρ ($g\ cm^{-3}$)	Particle equivalent diameter D_{BET} (nm)	Particle hydrodynamic diameter[a] D_{PCS} (nm)	Particle TEM diameter (nm)	XRD crystal size D_{XRD} (nm)
Pt–TiO_2	800	0.9	0.9	0.54	92	3.7	17.6	24	15–20	10

[a] On powder heated at 400 °C/3 h.

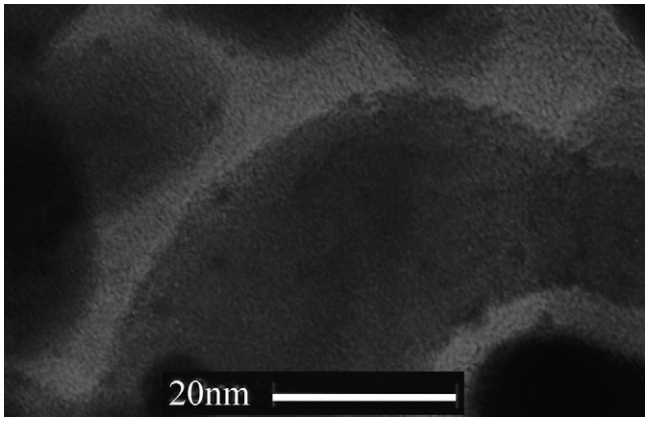

Fig. 2. TEM of the Pt–TiO_2 nanopowder, localization of Pt particles. Reprinted from Catalysis Today; H. Maskrot, Y. Leconte, N. Herlin-Boime, C. Reynaud, E. Guelou, L. Pinard, S. Valange, J. Barrault; Synthesis of nanostructured catalysts by laser pyrolysis; to be published; copyright (2006), with permission from Elsevier.

of 2–3 nm diameter (which appear darker on Fig. 2), lying on the TiO_2 surface. From this morphological point of view, the Pt–TiO_2 nanopowders obtained by laser pyrolysis appear very similar to the Pt–TiO_2 nanoparticles obtained by the flame synthesis method.[21]

From H_2-chemisorption, a Pt dispersion value of 45% is measured which indicates a mean platinum particle size of 2.6 nm, in good agreement with the value evaluated by TEM (Fig. 2).

The electrophoretic mobility is a function of both pH and ionic strength of the suspension; hence it is important to carefully monitor/control these parameters. The mobility (and therefore the zeta potential) of a suspension is directly related to the magnitude of the repulsive force between the particles. The greater the zeta potential the greater the repulsive force, therefore the lower the probability of aggregating particles. Knowing the isoelectric point (pHiep) allows an easy recovery of the flocculated powder; thereby preventing an undesired dispersion of the nanopowders in the environment. As a consequence, in a pH zone far from the pHiep, it is expected that the surface charges are sufficient to induce a repulsive force between the particles, leading to well dispersed suspensions. The solid loading can also influence the particle behavior. Fig. 3 shows the electrophoretic mobility versus pH and ionic strength for TiO_2–P25 and Pt–TiO_2. At pH < pHiep, the surface is positively charged, the positive sign of the mobility being due to the adsorption of H^+ onto the surface; conversely at high pH, protons are released from the surface, which explains the negative sign of the mobility.

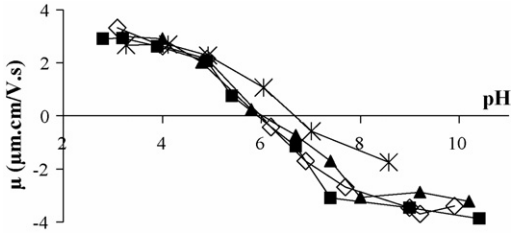

Fig. 3. Electrophoretic mobility vs. pH for TiO_2 P25 (∗) and for Pt–TiO_2 (◊ without electrolyte; ▲and ■ with KCl respectively, 10^{-2} and 10^{-3} M).

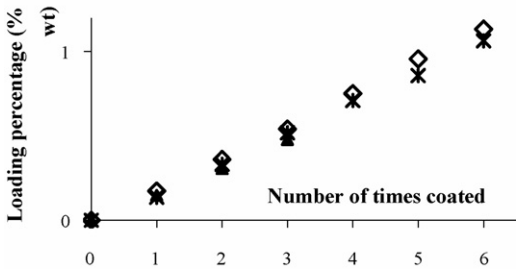

Fig. 4. Evolution of the Pt–TiO_2 loading (wt.%) vs. the number of dippings for three TiO_2 ceramic foams.

The pHiep (zero electrolyte concentration) of the TiO_2–P25 dispersions (pHiep = 6.7) is in good agreement with the literature values.[22–25] The pHiep of the Pt–TiO_2 suspensions are obtained at 6, independently of the presence of electrolyte (KCl). The ions (K^+ and Cl^-) added have a slight effect on the electrokinetic measurements, they allow us to evaluate the zeta potential using the Smoluchowski equation.[26]

3.2. Pt–TiO_2 nanopowder deposition on TiO_2 foam

The prepared suspension of Pt–TiO_2 (10 g/l) tends to be naturally acidic (pH around 4) so that it was decided to work at this acidic pH which is far enough from the pHiep. Ceramic foams were dipped in this stable suspension. The wt.% of catalyst immobilized increases linearly with the number of dippings (Fig. 4). The different slopes of the straight lines are due to the differences in the ceramic support surfaces. A weight loss observed during the thermal treatment illustrates the elimination of the carbonaceous species formed during pyrolysis.

Fig. 5a shows the structure (texture) of the ceramic foam used as support. Such texture is still well detectable after three dips followed by a thermal treatment (Fig. 5b). No important grain growth was observed (Fig. 5c) after annealing. The particle size is still in the nanometric range.

3.3. Catalysis: methanol oxidation

The preliminary catalytic results in methanol oxidation over Pt–TiO_2 nanopowders and their coating on ceramic TiO_2 foams are presented in Table 2. The ability of all the samples to favor the total elimination of methanol into CO_2 was evaluated and compared at 50% conversion.

The Pt–TiO_2 nanopowder synthesized by laser pyrolysis (0.54 wt.% Pt) was compared to a Pt/SiO_2 reference catalyst involving a similar Pt content (0.4 wt.% Pt). This Pt reference solid was prepared through a classical impregnation of a commercial silica (Aerosil D200, Degussa) with an aqueous solution of diaminodinitroplatinum(II), $[Pt(NH_3)_2(NO_2)_2]$. After impregnation, the solid was left to evaporate and dried at 100 °C in an oven, before annealing in air flow at 450 °C for 4 h.

The catalytic results reveal that the Pt–TiO_2 nanopowder synthesized by laser pyrolysis is more active than a conventional Pt/SiO_2 catalyst for the complete methanol decomposition into CO_2. Indeed, the methanol oxidation (50% conversion) over

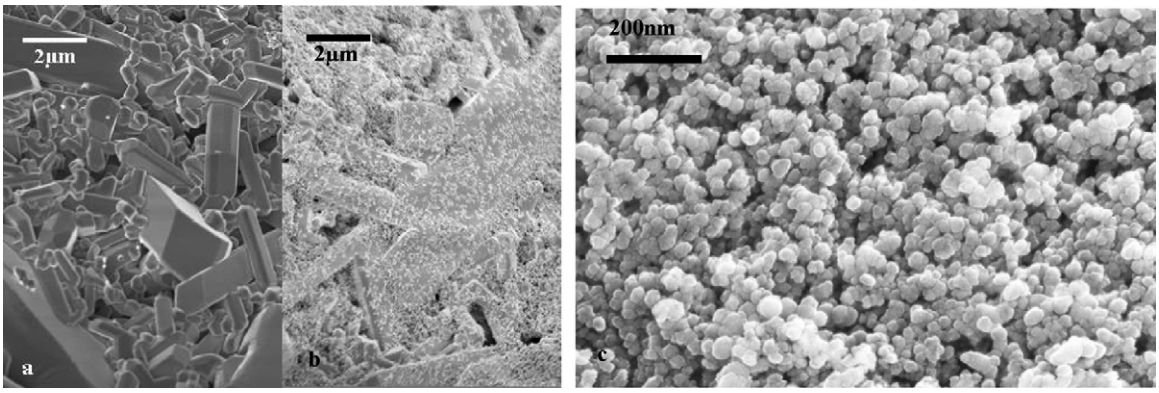

Fig. 5. Microstructure of the ceramic foam (a) before dipping; (b) after three dips and (c) after six dips, in the Pt–TiO_2 suspension (FE-SEM).

Pt–TiO_2 nanopowders occurs at a lower temperature (80 °C instead of 115 °C) than for Pt/SiO_2. This interesting result clearly demonstrates the possibility to generate by laser pyrolysis nanometric platinum particles well dispersed within the TiO_2 substrate, that reveal very active and selective in the total oxidation of MeOH into CO_2.

The next step consisted in evaluating the catalytic performances of a TiO_2 ceramic foam coated with Pt–TiO_2 nanopowders (Pt–TiO_2/TiO_2 foam-composites). The catalytic tests were first performed on the crushed ceramic composites, for a direct comparison with the nanopowders, then on the as prepared foam monoliths. It was first necessary to determine the MeOH oxidation theoretical temperatures at 50% conversion in order to check the absence of catalytic activity loss during the coating process.

These temperatures were determined by taking into account the Arrhenius law for a methanol activation energy (E_a) equal to 85 KJ mol^{-1}, considering as a reference the result obtained at 50% conversion for Pt–TiO_2 nanopowder synthesized by laser pyrolysis (see below).

$$K = A\mathrm{e}^{-E_a/RT}$$

$$\ln\left[\frac{(1-0.5)}{(0.5)\tau'}\right] = -\ln A + E_a/RT$$

considering that τ' is equal to the ratio of the amount of active metal and the flow rate

$$\tau' = m/Q \text{ with } m = \text{catalyst mass} \times \% \text{ metal}$$

$$\ln m - \ln Q = -\ln\ A + E_a/RT$$

The results (Table 2) indicated that the temperatures measured for the total oxidation of methanol are similar to those evaluated by taking into account the Arrhenius law, independently on the number of dippings.

The volatile organic compound elimination (deVOC) tests performed on these composites demonstrate that the dispersion of the nanopowders over the preformed ceramic does not modify their catalytic performances, thereby confirming that the dipping method used to coat the foam monoliths does not alter the active sites of the nanopowders synthesized by laser pyrolysis. The Pt–TiO_2 nanopowders and their coating onto ceramic foams therefore lead to very efficient catalysts for the total decomposition of methanol thereby showing that the shaping of these materials could be envisaged for industrial applications.

4. Conclusions

Laser pyrolysis allowed the preparation in one step of Pt–TiO_2 nanopowders, thereby demonstrating its potentiality as

Table 2
Preliminary catalytic results in methanol oxidation into CO_2 over Pt–TiO_2 nanopowders, over Pt–TiO_2/TiO_2 foam-composites and over a Pt/silica reference solid

Catalyst	Sample weight (mg)	Pt (wt.%)	T (°C)[a] theoretical	T (°C) at 50% methanol conversion
Pt/SiO_2 (Ref.)	50	0.4	–	115
Pt–TiO_2	50	0.54	–	80
Pt–TiO_2/TiO_2 foam-composite, (3 dippings) (crushed)	50	0.231×10^{-2}[b]	160	175
Pt–TiO_2/TiO_2 foam-composite, (3 dippings) (monolith)	380	0.231×10^{-2}[b]	125	125
Pt–TiO_2/TiO_2 foam-composite, (6 dippings) (crushed)	50	0.532×10^{-2}[b]	150	165
Pt–TiO_2/TiO_2 foam-composite, (6 dippings) (monolith)	450	0.532×10^{-2}[b]	110	115

[a] MeOH oxidation temperatures determined by taking into account the Arrhenius law (E_a = 85 KJ mol^{-1}) over Pt–TiO_2 nanopowders synthesized by laser pyrolysis as a reference (see text).

[b] The Pt content was theoretically evaluated from the number of dippings, considering the total mass of the composite (ceramic foam coated by Pt–TiO_2 nanopowders).

an original, versatile and efficient method for catalyst preparation. Such solids proved very efficient in catalyzing methanol oxidation into CO_2, showing their potentiality in being more widely used for the total oxidation of volatil organic compounds (deVOC).

The further deposition of Pt–TiO_2 nanopowders over TiO_2 ceramic foams by successive dippings led to Pt–TiO_2 (nanopowders)/TiO_2 (foam monolith)-composites that proved as active in MeOH oxidation as the initial Pt–TiO_2 phase but much easier to handle on a large scale in various industrial processes. Work is in progress to extend this original preparation method to other catalytic composites.

Acknowledgements

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