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Structured supports for noble catalytic metals: stainless steel fabrics and foils, and carbon fabrics

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Abstract

Conventional structured catalytic structures are constituted by a ceramic or metallic monolith whose wall surface is covered by a porous coating on which the active metal is deposited. To simplify the deposition procedures it is proposed to deposit the active metal on the bare surface of the carrier. The metal deposition is accomplished by the chemical reduction of metallic ions in aqueous solution. Catalytically active systems obtained by anchoring palladium (or ruthenium) on stainless steel supports or carbon fabrics are described. Their activity depends on the operating parameters of the deposition procedure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon fabrics; Stainless steel supports; Structured supports; Catalytic metals

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1. Introduction

In the case of catalytic polyphasic reactions (liquid–gas–solid), monolithic or ordered filled up reactors would present some advantages compared to the usual slurry or fixed bed reactors [1]: better reactant diffusion, better heat transfer, catalyst fixed on the monolith channel walls (elimination of the solid–liquid separation problems at the reactor outflow). However, the use of a structured catalyst in presence of liquid and gas phases imply to obtain a high loading of active catalyst particles strongly anchored on the support.

Some non-automobile catalytic applications of monolithic structures have been described in the literatures [1–3] and various manufacturers supply ceramic or metallic monoliths (Doduco, Corning, etc.). Typically, the channel walls of monoliths are covered by a porous oxide layer (mainly alumina) or carbon, on which the catalytic phase is deposited. This oxide layer has a large specific surface area which is supposed to allow a good dispersion of the active metal. However, the preparation of these monolith structures implies to master two unit operations: the deposition of the oxide layer on the whole channel wall surface and the deposition of the active metal on the oxide layer [1,3]. Due to the small size of channel aperture, flowing of viscous liquids or slurries in the monolith structure is not easy. The main problems are to obtained a good homogeneity of the oxide layer which must be strongly anchored on the carrier, and then an uniform active metal distribution on that layer throughout the monolith structure. Moreover, during further liquid phase reactions, the liquid flowing in the channels can erode the oxide coating or react with it.

To avoid these problems it could be interesting to deposit the metal rightly on the bare carrier surface [4]. Thus, we have studied the ways to deposit noble metals (Pd, Ru, Pt) on plane supports which could be then formed into monoliths or allow an ordered filling of a reactor. Two bi-dimensional materials which can be rolled spirally, corrugated, piled up, etc., after the

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metal deposition, have been selected: *stainless steel grids or foils*, and *carbon fabrics*. These supports have been chosen to achieve two different goals in order to apply structured catalysts to conversion of organic molecules in liquid phase:

- To replace the powdered active carbon carriers typically used under the form of slurry in triphasic hydrogenation reactions, by carbon fabrics which allow a well-ordered filling up of a reactor by the way of rolls or superposed layers (fixed bed reactor).
- To elaborate monoliths of various forms and sizes from stainless steel grids or sheets [5,6], and which could be used in organics hydrogenation reactions [4] (biphasic, gas–solid, and triphasic, gas–liquid–solid, reactions can be considered) or as hydrocarbon converters for hydrogen generation (hydrocarbon reforming, alcohol dehydrogenation, etc.).

Amongst the chemical processes [7] from which a metal can be deposited from an aqueous solution (immersion or displacement; contact; autocatalytic reduction), the autocatalytic one (electroless plating) which applies on conductor substrates as well on non-conductor [8] has been selected. Autocatalytic plating is defined as “*deposition of a metallic coating by controlled chemical reduction that is catalysed by the metal or alloy being deposited*” [9]. The deposition of metal is accomplished by the chemical reduction of metallic ions in an aqueous solution containing a reducing agent. The metal salt and the reductant agent react in the presence of a catalyst. The support material can be itself catalytic or be activated by deposits of a catalytic metal [10]. The metal to be deposited must be more noble (more electropositive) than the support. This redox process is similar to a galvanic process (anodic and cathodic reactions take place in the mechanism), the electron supply being the chemical reductant [10–12].

2. Experimental

2.1. Carriers and reactants

Stainless steel (SS) grids used are of 316L type (Spectra/Mesh), they are made of non-porous wires (diameter: 56 μm) and have square meshes (opening: 51 μm; open area: 42%). The calculated surface area of grids is 100 cm^2/g. Steel foils are of 316 type (Goodfellow), their thickness is 0.1 mm and their geometric surface area is 12.5 cm^2/g. Such materials have good mechanical properties and can be easily formed into monolithic structures.

Pd and Ru have been also deposited on other metallic grids (nickel, SS 304, nickel or chromium doped steels), but the best catalytic activities occur when metals are deposited on 316(L) SS.

Carbon (C) fabrics are commercial materials from CECA or Actitex. They are obtained by carbonisation of viscous fabrics (hydrogen consumption), followed by an activation treatment (porosity formation). The manufacturers do not disclose details on these treatments. Carbon fabrics have a high specific surface area (≈1000 m^2/g) and are microporous ($\bar{d} \approx 1\,nm$; $S_{micropores} \approx 660\,m^2/g$; $V_{micropores} \approx 0.45\,cm^3/g$).

Carbon fabrics have low mechanical properties, but use of carbon fabrics rolls is conceivable in small reactors or in pipes. The adsorbent properties of carbon fabrics (adsorption isotherms in a batch reactor and kinetics from in-line measurements in a filled column) have been evaluated from the adsorption of 4-chlorophenol and are described elsewhere [13]. Adsorption capacities of carbon fabrics are slightly better than those of a conventional active carbon (TE80 from Degussa) and could allow higher flow rates during the adsorption.

Palladium precursor is $PdCl_2$ (Janssen Chimica), ruthenium precursor is $RuCl_2$. The reductant agents are sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$, Fluka) or sodium borohydride ($NaBH_4$, Fluka). The other reactants (hydrochloric acid, acetone) are of high purity.

2.2. Preparation of catalytic systems

The autocatalytic deposition method has been detailed previously [4,14]. Carrier pieces are flat or have Z or U form; some handmade monoliths (9 × 9 × 9 mm, nine channels) have been also tested. The autocatalytic deposition process, operated in a stirred glass reactor, comprises five steps:

1. *Cleaning of samples* under reflux with acetone.
2. *Acid treatment of samples*: HCl 12 wt.%, 20 min, 333 K. Thorough rinsing (deionised water).

3. *Preparation of an aqueous $PdCl_2$ solution*: adding of hydrochloric acid (0.25–2 g HCl, 36 wt.% in 25 cm^3 of water, for 44 mg $PdCl_2$) is necessary to dissolve $PdCl_2$.
4. *Deposition of the metal* on the carbon clothes immersed in the $PdCl_2$ solution. A given volume of a reductant solution is added in well-controlled conditions (temperature: 298–353 K; reactant concentration; adding rate).
5. *Drying*: 2 h in air at 298 K.

This process leads to the zerovalent metal, catalytically active without activation treatment. The mechanism of the autocatalytic deposition is very complex [7,10,12], but it can be resumed by the following equation (metal precursor: $PdCl_2$; reductant: NaH_2PO_2):

$$2H_2PO_2{}^{2-} + 2H_2O + 2Pd^{2+} \rightarrow 2Pd^0 + H_2 + 4H^+ + 2HPO_3{}^{2-}$$

It is visually observed that the metal deposition occurs on the plane parts and on the folds of the Z or U samples. After the metal deposition, the flat pieces can be folded without loss of deposited metal.

The conventional impregnation method does not apply on SS, but applies on carbon fabrics and has been be used to deposit ruthenium [14]. In each deposition method the amount of metal precursor is calculated to lead to catalysts which would contain 5 wt.% of metal, if all the metal was really deposited.

2.3. Catalyst characterisation

Metal content is determined from ICP measurements. Specific surface areas of carbon fabrics are measured from nitrogen adsorption–desorption isotherms at 77 K (ASAP 2010).

The dispersion of palladium on C fabrics and SS supports was evaluated from hydrogen chemisorption (ASAP 2010C). For these non-conventional systems there is no indication on experimental conditions in the literature. So, the adopted conditions are: chemisorption temperature 353 K; pressure up to 53 kPa and ratio of $H/Pd = 1$ (further improvements could be required). In experimental conditions, hydrogen volume adsorbed by the supports is less than 0.1% of the volume adsorbed by the metal.

X-ray emission analysis have been performed in a scanning electron microscope coupled with an electron microprobe analyser.

2.4. Catalytic tests

The efficiency of catalyst preparation procedure is evaluated from the activity of the samples in a test reaction, hydrogenation of acetophenone (C_8H_8O), which is operated in a stirred semi-batch reactor (hydrogen pressure is maintained constant and equal to 25 MPa; temperature is 393 K; solvent: cyclohexane). Acetophenone molecule has an aromatic ring and a ketone function which can lead to different selectivities, depending on the active metal [15,16].

A depollution of waste water by hydrodechlorination of 4-chlorophenol on Ru/C fabrics catalysts has been also developed successfully [13], but is not described here.

3. Results and discussion

While Pd/SS grids or foils, Pd/C fabrics, and Ru/C fabrics have been prepared and studied the present work is focused on Pd/SS which is the most appropriate system to elaborate complex catalytic structures.

The properties of the metal deposited from the autocatalytic reduction method strongly depend on the preparation conditions [14]. X-ray emission measurements performed in a scanning electron microscope evidenced that metal deposits are palladium–phosphorus (or palladium–boron) alloys and can exist under two forms: (i) a thin film covering the whole carrier surface and (ii) discrete particles [14]. Deposition baths, whose composition corresponds to that of electroless plating baths, are stable and lead only to the formation of the thin film which is catalytically inactive. A very fast palladium precipitation rate occurs in "non-stable" deposition baths and metal particles do not deposit on the support, they aggregate and settle. Palladium deposits are catalytically active when palladium is under the form of discrete particles on the support surface. This is achieved with "metastable" deposition baths in which a slow reduction rate of the palladium salt leads to the formation of the thin palladium film on which small palladium particles deposit.

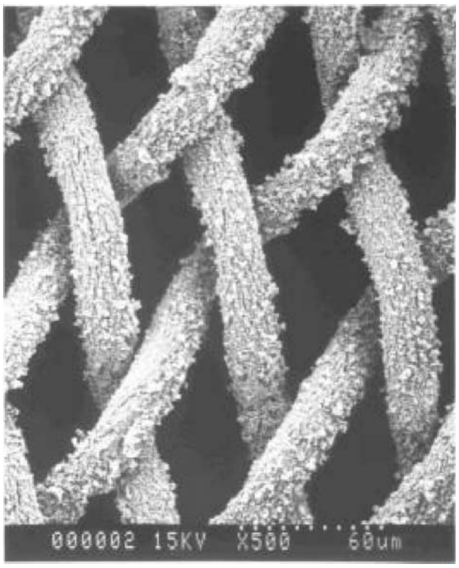

Fig. 1. Micrograph (SEM) of an SS grid covered with a film and particles of palladium.

Figs. 1 and 2 are micrographs (SEM) of a Pd/SS grid catalyst. Fig. 1 evidences the presence of large discrete palladium particles (3–10 µm) deposited on a continuous palladium film recovering the surface wires. Fig. 2 shows that these palladium particles are porous and result from the agglomeration (cauliflower-like), in a three-dimensional network of small spherical particles whose diameter is between 0.1 and 0.9 µm.

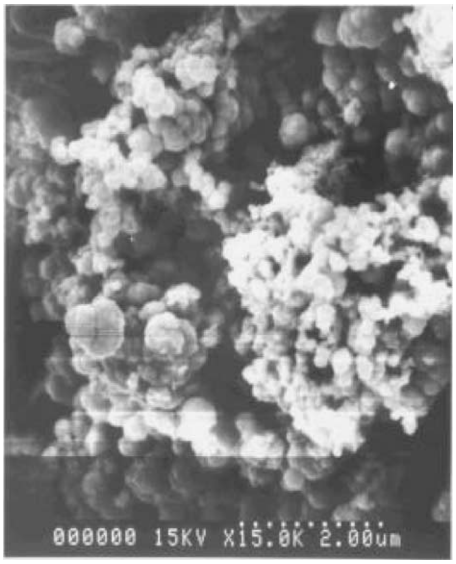

Fig. 2. Micrograph (SEM) of a large palladium particle deposited on an SS grid.

Table 1
Dispersion and catalytic activity of palladium particles deposited on different supports

Support	D_{Pd} (%)	S_{Pd} ($\mathrm{m^2/g_{Pd}}$)	$\bar{d}_{\mathrm{Pd}}$ (nm)	Ai (mol $\mathrm{H_2/g_{Pd}}$ h)
SS grids	9.1	40	18.8	24
SS grids	4	18	42.1	0
SS grids	13.5	60	12.5	63
SS grids	9	41	18.5	17
SS foils	6	5	15.6	18
SS foils	4.2	17.2	43.6	14
C fabrics	48.5	216	3.5	56
C fabrics	57	254	3	68

Otherwise, from chemisorption measurements presented in Table 1, the diameter of palladium particles deposited on SS grids is between 7.6 and 150 nm. Consequently, spherical particles, visible on Fig. 2, are probably formed by the agglomeration of small elementary palladium particles (fractal objects?).

From Table 1 it appears that catalytic activity is more or less related to the Pd dispersion for a given support. Pd dispersion on C fabrics is quite good (≈50%), which is not surprising since C fabrics have a very large surface area. The dispersion of Pd on SS supports is low (<15%), corresponding to the low surface area of these supports. In spite of this low Pd dispersion, Pd/SS grids can have the same catalytic activity than Pd/C fabrics. This could be attributed to interactions between the support and the active metal.

Measurements presented in Table 1 are related to non-reduced samples, degassed under vacuum at 393 K. Pd particles generated from the autocatalytic reduction method seem sensitive to sintering: an increasing of temperature degassing leads to a decreasing of Pd dispersion; hydrogen treatment is also detrimental to Pd dispersion. These effects are observed with Pd on SS supports and on C fabrics and leads to activity decreases.

The hydrogenation of acetophenone (AC) in the presence of palladium leads to the formation of phenylethanol (PE) which transforms in ethyl benzene (EB). With active catalysts the only product

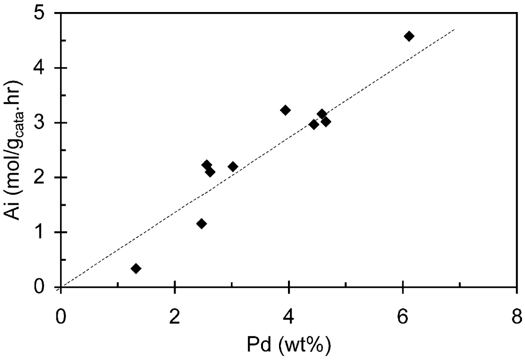

Fig. 3. Influence of Pd content on the catalytic activity expressed per gram of catalytic structure (SS grids).

detected at the end of the reaction (end of hydrogen consumption) is ethylbenzene. With less active catalysts, hydrogenolysis of phenylethanol is very slow, and phenylethanol and ethyl benzene are present.

Figs. 3 and 4 depict the initial activity (consumption hydrogen rate) of SS grids containing various palladium contents, in acetophenone hydrogenation.

The initial activity of catalytic systems, expressed per gram of catalyst is quite directly proportional to the palladium content (Fig. 3). Except for the lowest palladium contents, the initial activity expressed per gram of deposited palladium is quite constant (Fig. 4), which indicates that the palladium dispersion on the support remains the same when Pd content varies between 2.5 and 6.1 wt.%.

The percentage of Pd deposited on SS and the ratio of Pd/P depend on the preparation and operating parameters. On SS grids, 47–96% of palladium introduced in the bath is deposited, while it is 13–63% in the case of SS foils. The ratio of Pd/P varies between 21.3 and 35.7 for the Pd/SS grids structures. When sodium borohydride is used, the ratio of Pd/B varies from 31 to 397.

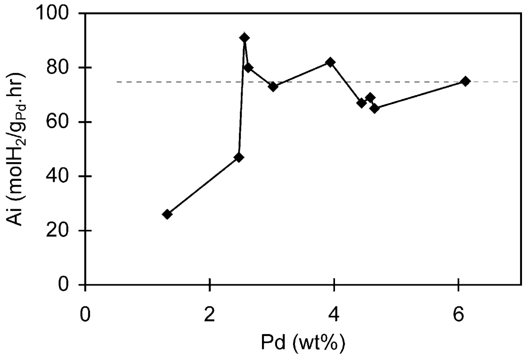

Fig. 4. Influence of Pd content on the catalytic activity expressed per gram of palladium (SS grids).

Table 2
Effect of HCl quantity, present in the deposition bath, on the catalytic activity of Pd/SS grids

HCl (g)	Bath pH	Pd (mg)	Percentage of Pd deposited[a]	Ai (mol H$_2$/g$_{Pd}$ h)
2	1.03	22.74	91	23
1	1.47	24	96	58
0.25	1.98	23.27	93	83
0.1	2.15	15.55	62	116
0	2.69	16.6	66	110

[a] 100% correspond to 25 mg of Pd.

It is more difficult to deposit Pd on SS foils than on grids and Pd deposited on foils is less active than Pd deposited on grids. It is assumed that is probably due to differences in the steel surface composition or constraints (we have not succeed to deposit Pd on annealed SS foils). Compared to grids, SS foils, except higher mechanical properties, have no advantages (less active, higher density per unit area, etc.), so SS grids have been preferred as support.

Catalytic activity can be affected by small amounts of poisons like phosphorus or chlorine. The presence of phosphorus and chlorine ions during the preparation could be damaging for the catalyst activity. The effect of hydrochloric acid amount added to dissolve $PdCl_2$ is illustrated by the results of Table 2.

When HCl quantity is increased (all other operating parameters remaining constant), the percentage of palladium deposited on the carrier is increased, but the initial activity of the catalytic structure is decreased. Palladium species deposited from the less acid baths are more active. As Cl^- ions are removed during grid washings, their influence occurs during the palladium deposition. It can be assumed that HCl acts on the formation rate of palladium particles, leading to larger particles less active. In spite of the detrimental action of HCl, $PdCl_2$ remains the more efficient palladium precursor to deposit palladium on SS surfaces.

The formation of the phosphorus–palladium alloy depending on several operating parameters is not easy to master, and its mechanism is not yet elucidated

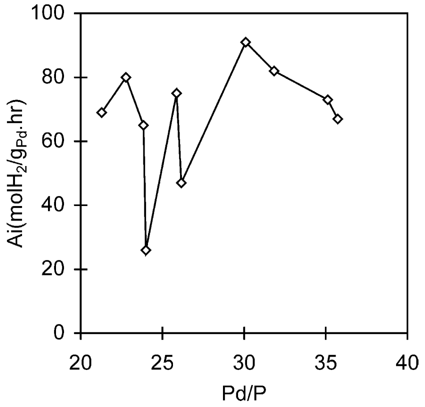

Fig. 5. Effect of the ratio of Pd/P on the catalytic activity of Pd/SS grids.

[7,10,12]. Effect of phosphorus on the activity of catalytic systems is complex. Fig. 5 depicts the effect of the ratio of Pd/P in Pd/SS grids (obtained from baths in which the hypophosphite amount was the same) on their initial activity. Obviously, the catalytic activity is not linked to the phosphorus content. But, for a given composition of deposition bath, an increase in the amount of hypophosphite used to reduce $PdCl_2$ leads to an increase in the catalytic activity as demonstrated by the results presented in Table 3.

If NaH_2PO_2 is replaced by $NaBH_4$, the PdB alloy formed has the same behaviour than the PdP alloy. However, the use of $NaBH_4$ as reductant is more difficult to master than NaH_2PO_2 use, it is more expensive, and does not lead to higher active catalysts.

Catalytic properties of Pd/C fabrics and Pd/SS grids have been compared to that of an industrial hydrogenation catalyst (Pd/C Degussa; 5% Pd; $\approx 1000\,m^2/g$). The results are presented in Table 4. When they are not prereduced by hydrogen, the three catalysts have similar initial activities but selectivities are different. Our catalysts leading to EB, while industrial catalyst produces only PE (no hydrogenolysis activity).

Table 3
Effect of hypophosphite amount on the catalytic properties of Pd/SS grids

$Q_{NaH_2PO_2}$ (ml)	Ai (mol H_2/g_{Pd} h)	PE	EB
53	11	48	46
75	14	27	73
95	23	23	77
115	29	0	100

Table 4
Comparison of initial activity and selectivities (after 30 min on stream) of commercial and laboratory Pd catalysts

Catalyst	Reduction (H_2, 393 K, 5 h)	Ai (mol H_2/g_{Pd} h)	PE (%)	EB (%)
Pd/active carbon	No	52	99	1
Pd/SS grids	No	72	0	100
Pd/C fabrics	No	68	0	100
Pd/active carbon	Yes	219	76	24
Pd/SS grids	Yes	48	0	100
Pd/C fabrics	Yes	42	15	85

A reducing pretreatment (H_2, 2 h, 393 K) decreases slightly the initial activity of Pd/C fabrics and Pd/SS catalysts (Pd dispersion is decreased), while initial activity of industrial catalyst is strongly enhanced. The surface metal complex of such catalyst must be decomposed in order to obtain the zerovalent active metal. Pd/C Degussa has a great hydrogenation activity (formation of PE), but a weak hydrogenolysis activity (formation of EB). Pd/SS grids and Pd/C fabrics lead to the formation of EB, their hydrogenolysis action is greater. This could be due to the presence of phosphorus, or/and metal support interactions.

4. Conclusion

The protective or decorative metal films obtained on various carriers from the electroless plating method are well known, but they are not catalytically active. Modifications introduced in the deposition procedure of this method lead to deposits of catalytically active metal particles on structured supports, like SS and carbon fabrics. The metal particles are strongly anchored on the support itself (no oxide layer) allowing a further formation of this system in large structures, like monoliths. The high surface area of carbon fabrics leads to a quite good dispersion of palladium on this support. SS grids have a very low surface area and palladium dispersion is poor, but palladium aggregates presents a surprisingly high activity. Although, the activity of these new catalytic systems is satisfactory, it has to be improved to reach the activity level of industrial catalysts.

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