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C. Jouannin, I. Dez, A.-C. Gaumont, J.-M. Taulemesse, Vincent Thierry, et al.. Palladium supported on alginate/ionic liquid highly porous monoliths: Application to 4-nitroaniline hydrogenation. *Applied Catalysis B: Environmental*, 2011, 103 (3-4), pp.444-452. 10.1016/j.apcatb.2011.02.008 . hal-03925162

HAL Id: hal-03925162

<https://normandie-univ.hal.science/hal-03925162v1>

Submitted on 26 Aug 2024

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Palladium supported on alginate/ionic liquid highly porous monoliths: Application to 4-nitroaniline hydrogenation

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A B S T R A C T

A catalytic system was designed in the form of highly porous monoliths (HPM) in order to be used in a continuous flow column reactor. This catalyst system was composed of an ionic liquid and a transition metal catalyst supported on a biopolymer matrix. Alginate was used as a natural support for immobilizing Cyphos IL-111 (an alkylphosphonium ionic liquid) and for Pd binding. The supported catalyst was efficiently used for the hydrogenation of 4-nitroaniline in the presence of either sodium formate or formic acid as the hydrogen donor. The catalytic HPM was elaborated using a combined procedure of solution icing and freeze-drying. The HPM could be used in a fixed-bed column system under "forced flux" (and recycling mode). The hydrogenation reaction, studied with solution recycling through the HPM, was mainly influenced by the flow rate in the column, the excess of hydrogen donor, the pH of the solution and the type of acid used for pH control (poisoning effect of chloride ions), but was poorly influenced by temperature. The hydrogenation reaction, in the single-pass mode, showed breakthrough curves of higher catalytic activity for HCOONa as hydrogen donor than for HCOOH.

Keywords:

Alginate
Phosphonium ionic liquid
Palladium
Hydrogenation
Sodium formate
Formic acid
Catalysis

1. Introduction

The development of supported ionic liquid phase (SILP) catalysts has recently retained a great deal of attention as a substituent to conventional supported (or heterogeneous) catalysts [1–5]. The immobilization of the catalyst at the surface of the supports allows to improve the recovery of the catalytic metal compared to homogeneous catalysis. Supports may consist in mineral surfaces (silica or alumina), zeolite, activated carbon, or polymers. For the last decade an increasing number of papers have been published investigating the use of biopolymers as support for catalysis [6–11]. However, the diffusion properties may restrict the accessibility of the substrate to reactive groups and the catalytic reaction rate. Additionally, the support may influence the regio- or stereo-selectivity of the reaction. These limitations may explain the increasing interest of research community for the development of SILP catalysis. Indeed, the ionic liquid (IL) phase behaves as a homogeneous phase with enhanced mass transfer properties while the immobilization of the phase at the surface of the support facilitates catalytic stability and catalyst recycling [12,13]. Initially, the supported liquid phase catalysts have been developed based on the concept of the heterogeneization of homogeneous catalysis. This

was based on the dissolving of target organometallic complexes in a small amount of a liquid phase dispersed as a thin film at the surface of the support [14]. One of the most important limitations of these processes was the leaching of the liquid phase due to the volatility of the solvent phase. This problem was faced using alternate solvents such as ionic liquids that combine both low volatility, good solubility for organic and mineral complexes [14,15]. Using ILs instead of conventional solvents makes profit of their low vapor pressure by decreasing the potential hazards and solvent loss. Optimizing the choice of the IL may help in recovering and separating the products of the reaction. Though conventional supports were initially used for the development of SILPs [16], the biopolymers have been recently tested as an alternative support [17,18]. The immobilization of the IL at the surface of a solid support allows a more efficient utilization of the IL and the catalyst since the IL's surface area is increased in comparison with its volume. It combines the interest of both homogeneous catalysis (high activity and selectivity) and heterogeneous catalysis (high specific surface area, recovery of the catalytic phase and separation of products for reactive phase, minimization of viscosity effects) [19]. Different processes can be used for the immobilization of the IL on the support: (a) the covalent attachment of the ionic liquid at the surface of the support, or (b) the physical and simple deposit of the ionic liquid phase containing target catalytic species at the surface of the support [20,21]. The review published by Gu and Li [14] gives a large overview of

the properties of these materials, the different concepts used for their synthesis. The IL immobilization generally proceeds through absorption/adsorption in the capillary network at the surface of the support. However, new trends have been recently proposed consisting in either: (a) grafting the IL at the surface of the support [22], or (b) immobilizing the IL in a biopolymer matrix [23]. A process was previously developed for the encapsulation of extractants and ionic liquids in alginate capsules for the production of a new generation of extractant impregnated resins (EIRs) [24–28]. These materials are able to bind metal anions (including chloro-complexes of catalytic metals such as Pd(II), Pt(IV) or Au(III)) in very acidic HCl solutions. Metal reduction may open the route for the use of a new type of supported IL catalysts.

Several studies have pointed out the importance to optimize the porous architecture of the biopolymer support for enhanced catalytic properties [18,29–32]. Improving the porosity of the support and the accessibility of the substrate to reactive groups enhances reaction kinetics for metal sorption and for catalysis. This can be obtained by designing specific biopolymer conditionings such as aerogels [30] or hollow fibers [33]. Biopolymer scaffolds have been prepared for improving macroporous properties (especially for medical applications) [34–39]. The elaboration of biopolymer highly porous monoliths (HPMs) consists in the dissolving of the biopolymer in an appropriate solvent and the freezing of the gel. The icing of water in the polymer network is followed by the freeze-drying (or the drying under supercritical CO₂ conditions) of the material, which leads to the formation of a macroporous network.

4-Nitroaniline is an intermediate in dye synthesis, antioxidants, pharmaceuticals, gum inhibitors and is also used as a corrosion inhibitor. The hydrogenation of 4-nitroaniline is a catalytic reaction easy to monitor by spectrophotometry [40].

A previous study was carried out for the elaboration of highly porous catalytic systems using alginate and chitosan as immobilizing biopolymer matrices, and tetraalkyl phosphonium ILs [23]. Several parameters were tested for the optimization of structural and catalytic properties, identifying more specifically the respective contributions of biopolymer characteristics, freezing temperature, coagulation agent, or the presence of cellulose fibers as mechanical strengthener. In the present work, the selected catalytic system is one of the best formulations obtained for HPM in the previous study: an alginate-based HPM supporting the ionic liquid Cyphos IL-111 and Pd as metal catalyst [23]. The present study focuses on the investigation of operating reaction parameters for the hydrogenation of 4-nitroaniline, such as flow rate in the dynamic system, substrate concentration, hydrogen type and concentration, pH of the solution, and temperature. The hydrogenation reaction proceeds in dynamic mode: the catalytic HPM was immobilized in a column reactor and the substrate solution was recirculated through the HPM. The catalytic system was characterized in terms of structure (by SEM observations), metal distribution (by SEM–EDX) and elemental analysis (by ICP–AES after mineralization) before being tested for catalytic purpose.

2. Materials and methods

2.1. Materials

Alginate sample was provided by Acros. The viscosity of the sample in water was measured using a Viscometer Visco Star Plus (Fungilab, Spain) at a polymer concentration of 1% (w/w): 485 mPa s. Cyphos IL-111 (tetradecyl(trihexyl)phosphonium tetrafluoroborate ionic liquid) was kindly supplied by Cytec (Canada). As pointed out above, the choice of phosphonium-based IL is due to the strong affinity of these phosphonium ionic liquids for binding chloro-palladate species through electrostatic attraction or ion

exchange properties [28]. The biopolymer-immobilized IL can be used for binding metal ions prior to metal reduction in the synthesis of Pd-supported catalysts. This is a different approach to that used with bmim-SILPs, where the solvation properties of the ILs are privileged [17]. This IL is solid at room temperature (melting temperature: 37 °C); it was used as supplied without any purification. Gelatin was supplied by VWR (France). Palladium chloride was purchased from Fluka AG (Switzerland) and zinc powder from J.T. Baker (France).

2.2. Synthesis of the catalytic system

The incorporation of the IL (Cyphos IL-111) in alginate gels was previously described for the synthesis of specific sorbents [26]. A similar procedure was used for the synthesis of alginate-based HPM. The gelatin was dissolved in hot water (50 °C) under agitation to reach a 20% (w/w) concentration. The solution of alginate (2%, w/w) was prepared in water. Sodium hydroxide (0.25 g of a 10 M solution) was added to 2.5 g of the 20% (w/w) solution of gelatin, which served as a “compatibilizing” agent that prevents the phase separation when the hydrophobic IL is added to the biopolymer solution [41]. Bradaric et al. [42] investigated the influence of the anion of ionic liquid on their properties. They showed that phosphonium salts are globally more hydrophobic than ammonium salts because the cation part is less available for forming hydrogen bonds. In addition, Banerjee and Khanna [43] compared hydrophobic properties of a series of phosphonium ionic liquids (using a series of solutes, such as alkanes, alkenes, alkynes, alcohols and aromatic compounds) with the structure of anion counterpart. They point out the high efficiency of BF₄-phosphonium salt for benzene/alcohol separation based on the balance between hydrophilic/hydrophobic properties of the IL. The amount of IL added to the solution was 2.5% (w/w). The alginate solution (2% w/w in water) was added to the mixture for a final composite volume of 50 mL. It was necessary to maintain the mixture at 50 °C to prevent the solidification of the IL before the molding of the foams. NaHCO₃ was introduced in the mixture as a porogen. The reaction of sodium carbonate with HCl will cause the *in situ* production of CO₂. The bubbles may contribute to improve the porosity of the material.

The next step consisted in the distribution of the viscous solution in moulds (plate formed of cylindrical holes of 10 mm height and 10 mm diameter) that were maintained for 1 h at –78 °C. The frozen cylinders were then removed from the moulds and dropped in a coagulation bath containing 0.5 M HCl solution at the temperature of 1 °C (container surrounded by crushed ice) for 10 h. Finally, the foams (HPMs) were rinsed with tap water (i.e. in the slight presence of calcium to prevent foam “destruction”, calcium contributing to cross-link the gel) and freeze-dried with a Alpha 1–4 LD freeze-dryer (Christ, Sigma).

The sorption of palladium was operated by contact under soft agitation (120 rpm) for 2 days of the HPMs with a 150 ppm solution of palladium chloride solution at pH 1 (controlled with HCl solution).

The reduction was operated by *in situ* produced hydrogen: the Pd(II)-HPMs were immersed in a 0.5 M H₂SO₄ solution in the presence of zinc powder for 24 h at ambient temperature under agitation (for improving diffusion of hydrogen gas till the center of the foams). The Pd⁰-HPMs were then rinsed with water and dried by freeze-drying.

2.3. Characterization of the catalytic system

Scanning Electron Microscopy (SEM) and SEM–EDX (SEM coupled with energy dispersive X-ray analysis) were performed using an Environmental Scanning Electron Microscope (ESEM) Quanta

FEG 200, equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system. The system can be used to acquire qualitative or quantitative spot analyses. The SEM observation was performed on the cross-section of the catalytic HPM (obtained by cutting with a thin-slice cutter). The topography of the samples was observed using secondary electron signal, while the backscattered electrons were used for the identification and localization of heavy metals at the surface of the materials (by phase contrast). SEM-EDX facilities were used for the analysis of specific zones at the surface of the HPMs.

In order to evaluate the amount of IL and Pd immobilized on the catalysts, the HPMs were mineralized in triplicate [28]: the HPMs were digested using 2 mL of 18 M H₂SO₄ under heating. In a second step, hydrogen peroxide (successive additions of 1 mL) was reacted with the acid mixture to improve the degradation of the HPM: hydrogen peroxide is added step-by-step till complete discoloration of the solution. After volume adjustment the solution was analyzed by an ICP-AES spectrophotometer (inductively coupled plasma atomic emission spectrometer) Jobin-Yvon Activa-M (Jobin-Yvon, Longjumeau, France) for the determination of the amount of P, B and Pd. The P element is used as a tracer of the ionic liquid cation, and B element as a tracer of the IL anion.

A pycnometer was used to evaluate the free volume of cylindrical foams; the void volume was close to 90% for these alginate-based IL-HPMs.

2.4. Catalytic reaction

The study of the catalytic activity of HPM-supported Pd catalyst was carried out on the hydrogenation of 4-nitroaniline (4-NA) in the presence of formic acid or sodium formate as hydrogen donor. The substrate was converted into *p*-phenylenediamine. The volume of substrate solution was 25 mL (initial concentration: 25 mg L⁻¹, 0.18 mM, in most cases) and the addition of hydrogen donor corresponded to 0.5 mL of formic acid (99% w/w), except when varied for investigating the effect of this parameter. The solution was maintained under agitation by a magnetic stirrer. The temperature of the reactor was maintained constant during the experiment by using a temperature-controlled box. The HPM catalyst was immobilized in a column, blocked by inert synthetic foam (Fig. AM1, Additional Material Section). The column was fed by a pump and the solution was continuously re-circulated through the column at a given flow rate (14 mL min⁻¹, except for the study of this parameter). An auxiliary recirculation loop was used for the analysis of the solution: the solution in the beaker was circulated at the flow rate of 12 mL min⁻¹ through a circulating-cuvette to measure on-line the absorbance of the solution at 381 nm with a spectrophotometer UV-1650PC (Shimadzu). UV and IR spectra of substrate and products showed that their respective analytical peaks were sufficiently separated and the measurement of the absorbance at 381 nm resolved to efficiently evaluate the concentration of 4-NA.

The efficiency of the catalytic system in the different reactions was compared by the half-reaction-time (HRT) and by the TOF (turn-over-frequency, mol 4-NA mol Pd⁻¹ min⁻¹) measured at the HRT (TOF@HRT). The TOF was determined taking into account the mass balance on substrate concentration, the reaction time and the amount of Pd on the catalytic HPM.

3. Results and discussion

3.1. Catalyst characterization

SEM observations were performed on the cross-section of the catalytic HPM in order to determine the structure of the material (porosity), and SEM-EDX analysis gave information on

the distribution of the ionic liquid and Pd within the alginate matrix.

The SEM photographs of catalytic HPM cross-section, at different growing magnitude, show that the macrostructure of the HPM is formed of elongated pores (length: 400–600 μm, and width: 5–10 μm, in most cases) (Fig. 1a). The shape of pores in alginate scaffolds is controlled by the freezing temperature of the polymer solution [34,35] and the mode of cooling (fast versus slow) [39]. Increasing the freezing temperature is supposed to increase the size of pores [34]. On the other hand fast cooling induces directional freezing and non-simultaneous ice nucleation due to large temperature gradients, while in slow cooling mode ice nucleation occurs simultaneously and leads to isotropic pore structures [39]. The morphology of pores is controlled by heat transfer during the synthesis of the biopolymer HPM [36,38]. The morphology of pores suggests that the present materials correspond to the one obtained for fast cooling process: the composite polymer solution (including alginate, gelatin and IL as a viscous solution) is set in the freeze at -78 °C without temperature ramp and the icing probably occurs non-homogeneously leading to orientated structures. Additionally, the readily free filtration of water through the cylindrical foams indicates that the HPM has interconnected pores.

The backscattered electron-photograph allows to identify the densest elements that appear as white spots on the image. The dense element, Pd, appears at the surface of HPM (Fig. 1b–d). The IL forms small ellipsoidal vesicles of 5–10 μm. A section of the vesicle (see Fig. 1d) shows a dense distribution of white dots (i.e., Pd element) on the layer of the vesicle. The Pd crystals are agglomerated at the interface of IL-biopolymer foams and remain in direct contact with the substrate solution.

The SEM-EDX analysis were performed on two different zones of the Pd-IL-alginate HPM: "Spectre 1" focuses the analysis on an IL vesicle (white area), while "Spectre 2" shows the analysis of a non-specific zone (grey area) (Fig. 2). On the unspecific zone, the analysis is representative of the organic material with small amounts of Pd element, P element (tracer of the IL cation), but also S and Zn elements (representative of sulfuric acid and zinc powder used for the *in situ* production of hydrogen, in the metal reduction step). This may cause partial catalyst poisoning. However, the amounts are probably not high enough to inhibit catalytic activity. The difference in the intensity of S peak between Spectre 1 (IL vesicle) and Spectre 2 (encapsulating material) is due to different affinity of the matrix and the IL for sulfate ions and sulfuric acid. The ratios Pd/S and P/S for Spectre 1 (IL vesicle) are significantly higher than those found for Spectre 2 (embedding matrix): sulfuric acid and Zn have more relative affinity for matrix biopolymers than for IL.

On the vesicle zone, the proportion of P and Pd elements is much more important than on the unspecific zone. The intensities should be considered as indicative data (non-quantitative) since the focus of electron beam does not allow to restrict the analysis to a fine spot but analyses a small volume around the spot. However, the difference in intensities between the two spectra appears to be representative of the difference of ionic liquid presence between vesicle and biopolymer matrix: a small fraction of IL is included in the polymer matrix but the highest IL loading is localized in the vesicles. Small amounts of Pd(II) can be probably bound (and further reduced) on alginate material since the sorption proceeds at pH 1 (lower pH would considerably reduce the potentiality of the biopolymer to bind Pd(II)). However, the main part of immobilized Pd is located on IL vesicles.

The mineralization of the HPM, followed by the analysis of the obtained solutions by ICP-AES allowed to quantify the amount of Pd and IL immobilized on the catalytic materials: close to 63 mg Pd g⁻¹ HPM and 28 mg IL g⁻¹ HPM. The average weight of dried catalytic HPM was 27 mg: the amount of Pd per HPM is thus 1.5 × 10⁻⁵ mol. The molar ratio Pd/IL was close to 0.66. The molar ratio is slightly in

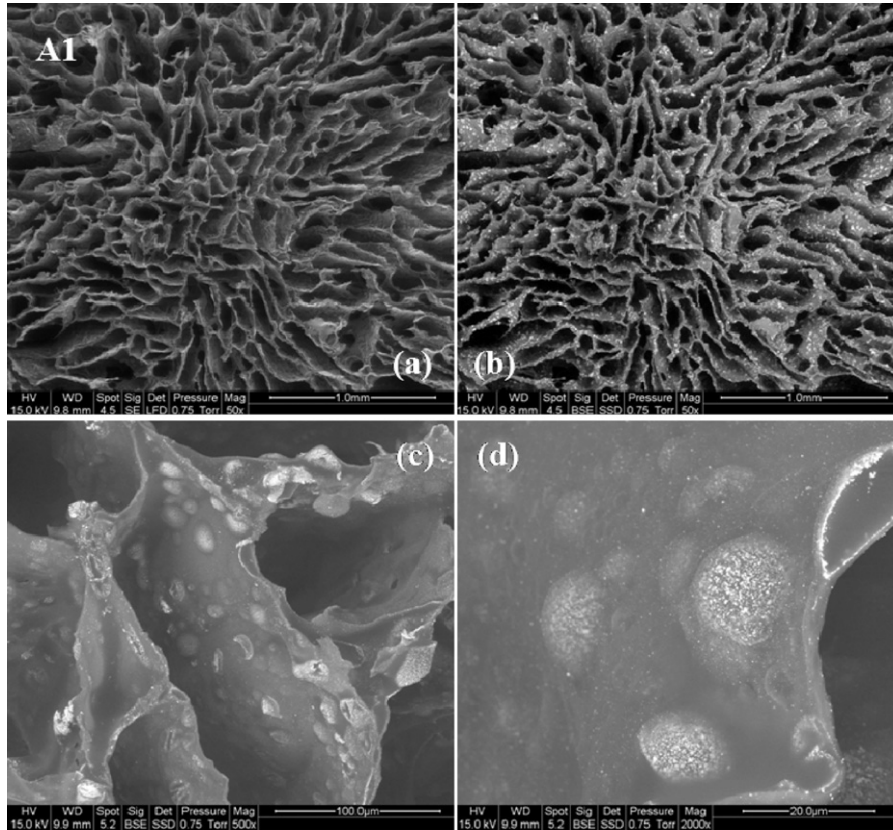


Fig. 1. SEM photographs of Pd-supported IL alginate HPM (bar scale: (a) and (b) 1 mm, (c) 100 μm and (d): 20 μm; (a): secondary electrons for morphology observations; (b-d) backscattered electrons for phase contrast determination of heavy elements).

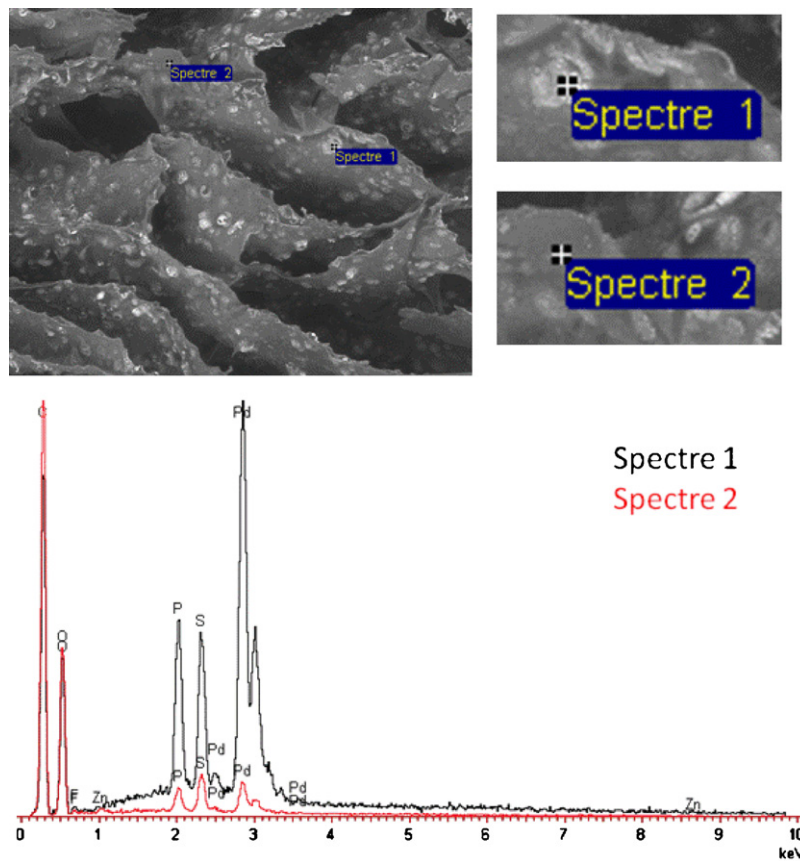


Fig. 2. SEM-EDX analysis of specific zones of Pd-supported IL alginate HPM.

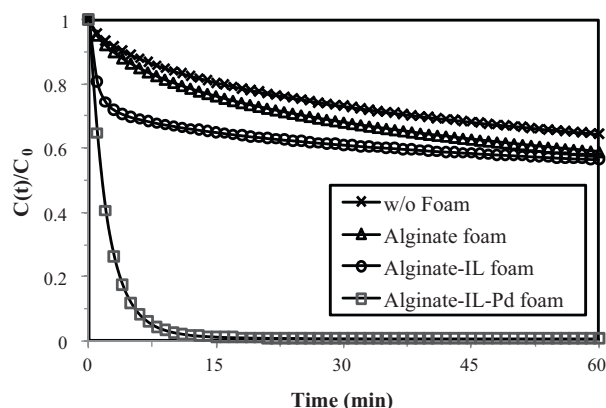


Fig. 3. Influence of foam type on the catalytic hydrogenation of 4-NA ([4-NA]: 25 mg L⁻¹; pH 2; T: 25 °C; hydrogen donor: 0.5 M HCOOH; flow rate: 14 mL min⁻¹).

excess compared to the expected stoichiometry (1:2) for the binding of palladium (PdCl₄²⁻) to the cation of the IL (R₃R'P⁺) [28]. This probably means that a fraction of the metal was bound to the biopolymer matrix at pH 1. In previous studies, the sorption of Pd(II) on Cyphos IL-101-alginate beads was determined in 1 M HCl solutions: these acidic conditions are too strong to allow alginate to significantly bind the metal. A tentative explanation could deal with the possible agglomeration of Pd around bound Pd(II) by a nucleation phenomenon or a change in the molar ratio after metal reduction due to possible degradation of organic compounds.

3.2. Effect of operating reaction parameters on hydrogenation kinetics

3.2.1. Influence of the support on hydrogenation kinetics

In order to evaluate the actual contribution of each component of the catalytic HPM on the hydrogenation kinetics, different HPM with or without IL and Pd (alginate HPM, alginate/IL-HPM and alginate/IL/Pd-HPM) were tested under the same experimental conditions (Fig. 3). Even without any HPM in the reactor, a decrease of the concentration of the substrate in the presence of formic acid is observed. However, the concentration decrease is very slow and even after running for 60 min the conversion does not reach 40%. In the presence of alginate HPM (without IL or Pd), the evolution of the substrate concentration follows a similar trend: the concentration being slightly lower, this probably means that a small sorption of the 4-NA occurs at the surface of alginate HPM. In the presence of the IL supported on the alginate HPM (alginate/IL-HPM, without Pd), the substrate concentration at equilibrium is close to the residual concentration achieved with alginate HPM after 60 min (removal yield close to 43%, Table 1). However, the initial decrease of the substrate concentration was much faster. Additionally, the IL-alginate HPM turns its color from white to yellowish at the end of the reaction but recovers its initial white color when washed up with slightly acid water. The decrease of the substrate concentra-

Table 1
Kinetic parameters for the hydrogenation of 4-NA—Impact of the type of foam.

Type of foam	Conversion yield ^a (%)	Half reaction time ^b (s)	TOF@HRT
No foam	36	750	–
Alginate foam	41	650	–
Alginate-IL foam	43	210	–
Alginate-IL-Pd foam	100	97	0.175

TOF@HRT: mol 4-NA mol⁻¹ Pd min⁻¹.

^a At 60 min if conversion is not complete.

^b Half reaction time corresponds to the half of the substrate elimination at 60 min (when conversion is not complete).

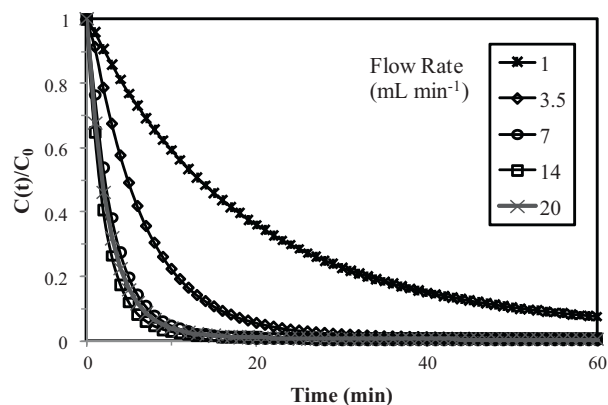


Fig. 4. Influence of flow rate on the catalytic hydrogenation of 4-NA ([4-NA]: 25 mg L⁻¹; pH 2; T: 25 °C; hydrogen donor: 0.5 M HCOOH; catalyst: Alginate-IL-Pd HPM).

tion can probably be explained by the absorption of the substrate on the IL vesicles at the surface of the HPM. The incorporation of Pd on the IL-alginate HPM (alginate/IL/Pd-HPM) substantially improves the conversion yield and the complete hydrogenation of 4-NA is achieved in less than 15 min. This preliminary experiment confirms the catalytic efficiency of the composite Pd-IL-Alginate HPM.

3.2.2. Influence of the flow rate on hydrogenation kinetics

The dynamic mode in column system induces hydrodynamic parameters with potential impact on mass transfer and reaction rate. In order to verify the contribution of hydrodynamic characteristics, the flow rate is varied. Increasing the flow rate in the column increases the flux velocity in the porosity of the HPM (under forced conduction) and decreases the mean residence time (compensated by the recirculation of the fluid in terms of cumulative residence time). Fig. 4 shows that the “forced regime” (i.e., high flow rate and high superficial velocity) with flow rate above 7 mL min⁻¹ is more favorable for the catalytic hydrogenation of 4-NA. At low flow rate (i.e., 1 mL min⁻¹, corresponding to a superficial velocity close to 0.2 m min⁻¹) the hydrodynamic regime is not appropriate and even after 60 min the conversion is not complete (close to 92%). When increasing the flow rate, the hydrogenation kinetics increases. At a flow rate of 3.5 mL min⁻¹, the complete conversion is achieved but it is necessary to increase the flow rate up to 7 mL min⁻¹ to reach the stationary mode. The differences in the kinetics profiles are poorly significant in the range 7–20 mL min⁻¹ (i.e., superficial velocity: 1.4–4 m min⁻¹). This is confirmed in Table 2 by the comparison of half reaction times (HRTs) and TOF@HRT (turnover frequency calculated at HRT). The HRT decreases until a flow rate of 7 mL min⁻¹ before tending to stabilize. A reciprocal trend is observed with TOF@HRT, which increases with flow rate and stabilizes above 7 mL min⁻¹. The flow rate of 14 mL min⁻¹ (i.e., superficial velocity ≈ 3 m min⁻¹) is used for the other experiments.

Table 2
Kinetic parameters for the hydrogenation of 4-NA—Effect of flow rate in the column.

Flow rate (mL min ⁻¹)	Conversion yield ^a (%)	Half reaction time ^b (s)	TOF@HRT (mol 4-NA mol ⁻¹ Pd min ⁻¹)
1	92	720	0.024
3.5	99	291	0.058
7	100	135	0.126
14	100	97	0.175
20	100	109	0.156

TOF@HRT: mol 4-NA mol⁻¹ Pd min⁻¹.

^a At 60 min if conversion is not complete.

^b Half reaction time corresponds to the half of the substrate elimination at 60 min (when conversion is not complete).

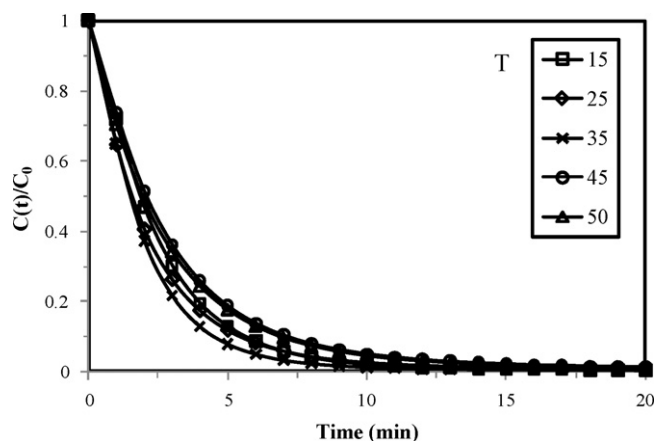


Fig. 5. Influence of temperature (T , °C) on the catalytic hydrogenation of 4-NA ([4-NA]: 25 mg L^{-1} ; pH 2; hydrogen donor: 0.5 M HCOOH ; catalyst: Alginate-IL-Pd HPM; flow rate: 14 mL min^{-1}).

3.2.3. Influence of the temperature on hydrogenation kinetics

It is a well-known fact that temperature can influence most catalytic reactions, such as the hydrogenation of 4-nitrophenol [44]. Additionally, the ionic liquid Cyphos IL-111, which is part of the HPM, has a melting temperature of 37°C ; thus the phase change of the IL with increasing temperature may affect the catalytic HPM. Fig. 5 and Table 3 show that the temperature of the reaction hardly affects the hydrogenation of 4-NA in the range $15\text{--}50^\circ\text{C}$. The IL is stable on a large range of temperature; this is not the case for biopolymers that can be partially degraded above temperatures such as 150°C , although the association with ILs may increase their thermal stability. Anyway, the main objective of the study focuses on the test of catalytic properties under low temperature and low energy conditions.

No significant changes are observed when the temperature is above the IL melting point. The Pd micro- or nano-particles are located in the vesicles and after metal reduction they appear on the internal periphery of the vesicles at the interface with biopolymer encapsulating material, as presented in the previous section on the catalyst characterization with SEM analysis. The encapsulation of the IL in the biopolymer may affect the melting properties of the IL, which, in turn, makes debatable the determination of the physical state of the IL around 35°C in the vesicles. Anyway, the possible change of the IL state does not appear to influence the availability and accessibility to reactive catalytic sites.

3.2.4. Influence of the hydrogen donor (type and concentration) on hydrogenation kinetics

The hydrogen donor used in this study, formic acid, can be provided in two forms: acidic form and salt form (adjusting the pH to $\text{pH } 2 \pm 0.1$). Additionally, it is important to evaluate the excess of hydrogen required to reach the complete conversion of the substrate. The effect of a variation of both the type and the concentration of the hydrogen donor is analyzed through Fig. 6. In the case of HCOOH, the increase of the concentration of hydro-

Table 3

Kinetic parameters for the hydrogenation of 4-NA—Effect of temperature.

Temperature (°C)	Conversion yield (%)	Half reaction time (min)	TOF@HRT
15	100	113	0.150
25	100	97	0.175
35	100	92	0.184
45	100	125	0.136
50	100	117	0.145

TOF@HRT: $\text{mol 4-NA mol}^{-1} \text{ Pd min}^{-1}$.

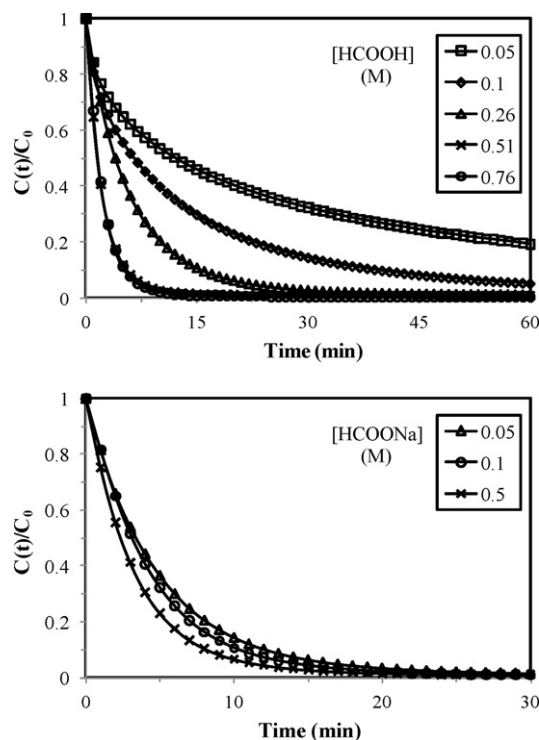


Fig. 6. Influence of hydrogen donor (type and concentration) on the catalytic hydrogenation of 4-NA ([4-NA]: 25 mg L^{-1} ; pH 2; T : 25°C ; catalyst: Alginate-IL-Pd HPM; flow rate: 14 mL min^{-1}).

gen donor improves the kinetics of hydrogenation. A minimum concentration of 0.1 M is required to reach the full conversion of the substrate. Above a concentration of 0.5 M HCOOH , the conversion kinetics reaches an optimum, and, increasing hydrogen donor concentration does not change the reaction rate. Table 4 confirms these trends: both the HRT and the TOF@HRT reach an optimum at the concentration of 0.5 M before stabilizing. Substantial differences are observed when using HCOONa: the concentration of the hydrogen donor has a much limited effect on the kinetic profile. Though a slight increase occurs at 0.5 M , the profiles are very close: the HRTs and the TOFs reach the same order of magnitude with limited variations around $3 \text{ min } (\pm 26 \text{ s})$ and $0.097 (\pm 0.016) \text{ mol 4-NA mol}^{-1} \text{ Pd min}^{-1}$, respectively. However, these values show that HCOOH is more efficient than HCOONa since the HRT is halved (close to 1.5 min) and the TOF increases up to $0.175 \text{ mol 4-NA mol}^{-1} \text{ Pd min}^{-1}$. This is confirmed by the time required to achieve complete conversion of the substrate: about 10 min for HCOOH and up to 20 min for HCOONa. The sodium formate is more

Table 4

Kinetic parameters for the hydrogenation of 4-NA—Effect of type of hydrogen donor (HD) and concentration of hydrogen donor ([HD]).

Type of HD	[HD] (M)	Conversion yield ^a (%)	Half reaction time ^b (min)	TOF@HRT
HCOOH	0.05	81	398	0.032
	0.1	95	346	0.044
	0.25	100	240	0.071
	0.5	100	97	0.175
	0.75	100	100	0.170
HCOONa	0.05	100	188	0.090
	0.1	100	205	0.083
	0.5	100	143	0.119

TOF@HRT: $\text{mol 4-NA mol}^{-1} \text{ Pd min}^{-1}$.

^a At 60 min if conversion is not complete.

^b Half reaction time corresponds to the half of the substrate elimination at 60 min (when conversion is not complete).

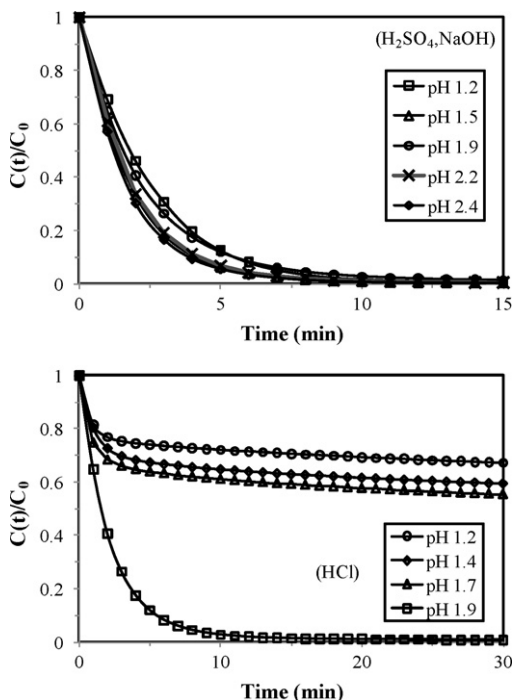


Fig. 7. Influence of pH (controlled with either $\text{H}_2\text{SO}_4/\text{NaOH}$ or HCl) on the catalytic hydrogenation of 4-NA ([4-NA]: 25 mg L^{-1} ; T : 25°C ; hydrogen donor: 0.5 M HCOOH ; catalyst: Alginate-IL-Pd HPM; flow rate: 14 mL min^{-1}).

efficient than formic acid at low concentration (below 0.3 M) but, at higher concentration, formic acid reveals more efficient. The active part of the hydrogen donor is HCOO^- . The difference in the behavior of the two reagents is probably dealing with the pH control which is required when using sodium formate.

3.2.5. Influence of the pH

In order to verify the suggested interpretation of the effect of type and concentration of the hydrogen donor, and to verify the sensitivity of the process to the pH of the solution, two series of experiments have been performed: changing the pH around the target value (i.e., pH 2) using two different acids (sulfuric acid and hydrochloric acid), and using NaOH for pH increase (Fig. 7). The kinetic profiles are substantially different when using HCl or H_2SO_4 for pH control. With sulfuric acid for pH control, the kinetic profiles (as shown in Table 5) hardly change: the TOF@HRT is close to the average value $0.192 \text{ mol 4-NA mol}^{-1} \text{ Pd min}^{-1}$ (standard error: 0.025). When using HCl for decreasing the pH, the reaction is almost inhibited: the equilibrium concentrations at 60 min (not shown in

Table 5
Kinetic parameters for the hydrogenation of 4-NA—Effect of pH and acid used for pH control (NaOH for pH increase, above 2).

Acid	pH	Conversion yield ^a (%)	Half reaction time ^b (s)	TOF@HRT
H_2SO_4	1.2	100	110	0.154
	1.5	100	82	0.207
	1.9	100	97	0.175
	2.2	100	84	0.202
	2.4	100	76	0.223
	HCl	1.2	36	58
1.4		45	111	0.069
1.7		49	53	0.157
1.9		100	97	0.175

TOF@HRT: $\text{mol 4-NA mol}^{-1} \text{ Pd min}^{-1}$.

^a At 60 min if conversion is not complete.

^b Half reaction time corresponds to the half of the substrate elimination at 60 min (when conversion is not complete).

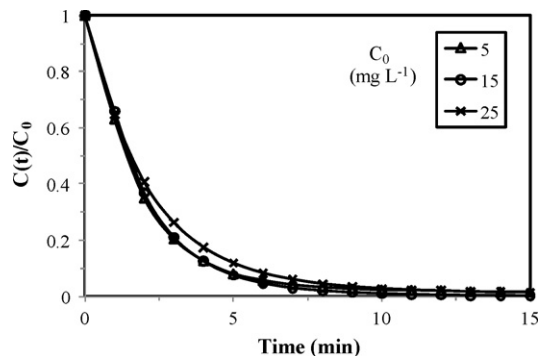


Fig. 8. Influence of substrate concentration on the catalytic hydrogenation of 4-NA (pH 2; T : 25°C ; hydrogen donor: 0.5 M HCOOH ; catalyst: Alginate-IL-Pd HPM; flow rate: 14 mL min^{-1}).

Fig. 5 but appearing in Table 5) show conversion yield lower than 50%. This means that the profiles for curves at pH 1.2–1.7 controlled with HCl are very close to those obtained with alginate and more specifically IL-Alginate HPMs (i.e., without Pd catalyst) both in terms of equilibrium values and kinetics. The presence of chloride ions is thus poisoning the hydrogenation catalyst or, at least, inhibiting the catalytic hydrogenation. The hydrogenation of hydrogen peroxide was found to be more and more inhibited with increasing chloride ion concentration [45]. From these experiments it appears that the pH should be controlled around 2 using sulfuric acid and that chloride ions should be prohibited to prevent possible poisoning of the catalyst.

3.2.6. Influence of the substrate concentration on hydrogenation kinetics

The concentration of the substrate was decreased from 25 to 5 mg 4-NA L^{-1} (Fig. 8 and Table 6). The kinetic curves overlap. The HRT does not change significantly with 4-NA concentration. The amount of hydrogen donor, in excess, is sufficient to achieve the complete conversion of the substrate. Increasing the relative excess of hydrogen donor (versus substrate) does not change the kinetic profile. This is consistent with the results shown in Fig. 7: above a relative excess of hydrogen donor, its concentration does not improve the catalytic efficiency. Since for all three concentrations the conversion was complete and the HRT approximately the same, logically the TOF@HRT linearly increased with substrate concentration.

3.2.7. Aging of the catalyst – use in non-recycling mode

In order to evaluate the efficiency of the catalyst for a long-term use, a complementary series of experiments is performed using the same type of Pd-IL-Alginate HPM immobilized in a column without solution recycling (single-pass mode), with much lower flow rate: 0.38 mL min^{-1} , corresponding to a mean contact time of 60s in the catalytic HPM. The outlet concentration is monitored on-line. Fig. 9 shows the time course of the outlet concentration for two hydrogen donors using either 0.5 M HCOOH or 0.1 M HCOONa . This figure clearly shows that sodium formate is more

Table 6
Kinetic parameters for the hydrogenation of 4-NA—Effect of substrate concentration (C_0).

C_0 (mg L^{-1})	Conversion yield (%)	Half reaction time (s)	TOF@HRT
5	100	88	0.039
15	100	93	0.109
25	100	97	0.175

TOF@HRT: $\text{mol 4-NA mol}^{-1} \text{ Pd min}^{-1}$.

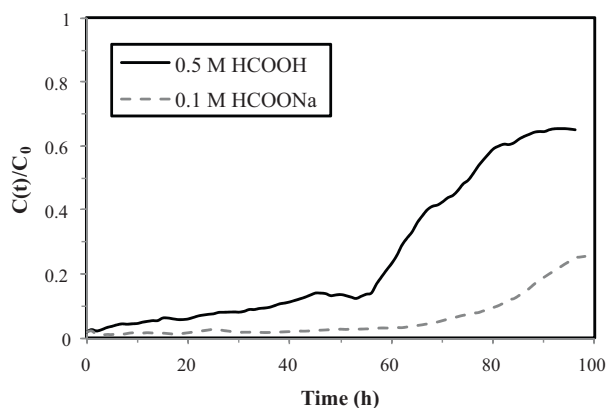


Fig. 9. Breakthrough curves for the hydrogenation of 4-NA using either 0.5 M HCOOH or 0.1 M HCOONa as the hydrogen donor (pH 2, controlled with H₂SO₄, flow rate: 0.38 mL min⁻¹; Pd loading: 0.77 mmol Pd g⁻¹).

efficient than formic acid. The increase of the outlet concentration is much slower with sodium formate: it maintains a conversion yield greater than 95% up to 68 h while the breakthrough occurs after 11 h with formic acid. This means that the catalytic HPM is able to hydrogenate up to 1.55 L of 4-NA solution at initial concentration 25 mg L⁻¹ (i.e. 39 mg substrate) before the catalyst begins to lose its efficiency with HCOONa. After 4 days of operating time, the conversion yield reaches 35% and 75% with HCOOH and HCOONa, respectively. In cumulative terms (over 4 days of operating time), the total conversion yields reach 74% and 93% for HCOOH and HCOONa, respectively. The TOF is calculated after 96 h of operating time (by integration of the breakthrough curve): 0.088 mol 4-NA mol⁻¹ Pd h⁻¹ for HCOOH and up to 0.206 mol 4-NA mol⁻¹ Pd h⁻¹ for HCOONa. These are other evidences that HCOONa is a more efficient hydrogen donor than HCOOH. At the same time, no leaching of the Pd on the outlet solutions is observed by ICP-AES analyses, which confirms the stability of the catalysts.

The alginate material is quite stable under selected experimental conditions (weak acidity) and the IL can readily support the same conditions. The experiments performed on a continuous mode for contact times greater than 3 days showed a decrease of catalytic efficiency after 2 days. However, it was not possible identifying the main reason for the decrease of catalytic performance. For long exposure to highly acidic conditions it is probably not possible rejecting the possibility that a part of the metal could be released. But under selected experimental conditions it was not possible detecting substantial loss of metal.

Though the immobilization of the IL is quite stable as shown on previous studies of metal sorption using similar immobilization techniques, it is not possible totally rejecting the release of traces of ILs that could alter the composition of the catalyst and its interactions with the substrate solution. This could contribute to explain the progressive loss of activity of the catalyst observed in Fig. 9.

4. Conclusion

The synthesis procedure, using the combined icing/freeze-drying procedure, allows to design alginate-based HPM with stable immobilization of ionic liquid in the biopolymer matrix, followed by Pd(II) sorption and metal reduction. The catalytic HPM shows very opened structure by SEM observation with a highly porous network. The SEM-EDX analysis shows the presence of IL vesicles with higher density of both IL and Pd compared to biopolymer matrix. The study of the catalytic HPM in fixed-bed column system under "forced flow" (and recycling mode) shows good catalytic efficiency for the hydrogenation of 4-nitroaniline in the presence of a hydrogen donor such as formic acid (or sodium formate). A min-

imum flow rate should be used to reach a high efficiency of the catalyst (forced flow for a superficial velocity of 1.4 m min⁻¹). The half reaction time strongly depends on hydrogen donor concentration (especially in the case of formic acid) and the pH (close to 2), but is also strongly dependent on the type of acid used for decreasing the pH. A large excess of hydrogen donor is required for achieving the complete conversion of the substrate; however, above this limit excess of hydrogen donor (0.5 M for HCOOH, lower for HCOONa) this parameter no more influences hydrogenation reaction. The pH hardly influences hydrogenation reaction in the range 1.2–2.4 when controlled with sulfuric acid. Nevertheless, decreasing the pH below 1.9 with hydrochloric acid inhibits the hydrogenation of 4-nitroaniline. Chloride ions are strongly poisoning the catalyst. The influence of temperature (in the range 15–50 °C) is negligible. The catalytic HPM is also successfully tested at a lower flow rate in the single-pass mode for evaluating the efficiency of the catalyst at long-term (4 days) in order to evaluate the aging of the catalyst: 0.1 M HCOONa is more efficient than 0.5 M HCOOH as the hydrogen donor. It allows to maintain efficient catalytic performance for 68 h (conversion yield higher than 95%).

Acknowledgements

The financial support from Agence Nationale de la Recherche to the BiopSIL project (ANR-08-CP2D-02) is greatly acknowledged. Cytec (Canada) is acknowledged for kindly supplying the Cyphos IL-111 sample.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2011.02.008.

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