Electroactive polymers as novel supports:
Properties of Pd-Sn catalysts supported over polypyrrole or polyaniline for application in water treatment.

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Introduction

Polymers represent a class of materials that play a role of growing importance in catalysis, due to the possibility of controlling in a simple way their morphology and their physico-chemical properties[1]. Recently, electroactive polymers such as polypyrrole or polyaniline have been used as supports for dispersing noble metals such as palladium[2-5]. Polypyrrole or polyaniline could be advantageously used as support for their important conductivity, their redox and acido-basic properties and their stability. For example, depending on the experimental conditions, the impregnation of palladium precursor salt on this type of polymer can directly lead to the incorporation of Pd° in the polymer matrix. The applications of this type of catalysts are reactions performed at low temperature (<100°C), such as hydrogenation of nitrobenzene, acetophenone, or nitrate. In some cases, the catalytic performances of these catalysts are better than that of their counterpart deposited on classical supports, and one of the . The aim of this presentation is to show that the use of polypyrrole (PPy) or polyaniline(Pani) as support for Pd-Sn systems leads to much higher activity and selectivity for nitrate reduction than those obtained with a classical Pd-Sn/Al₂O₃ catalyst. It will be demonstrated that the good catalytic performances are mainly due to the ion-exchange properties of the support, linked to the oxidation state of the polymer.

Materials and Methods

The supports were prepared by oxidation of the monomer. The experimental conditions were chosen as a function of the literature data in order to obtain the best conductivity of the polymer. Polymerization conditions are reported in table 1. After washing and drying of support, the Pd-Sn catalysts were prepared by successive impregnation or co-impregnation of the support by the precursor salts ($PdCl_2$ and $SnCl_4$). After washing and drying, catalysts were directly used for nitrate reduction or activated by reduction at 110°C. Nitrite and nitrate reduction was performed in water at 25°C and under hydrogen. Catalysts were characterized by TEM, XRD, FTIR and elemental analysis

Table 1 : Polymerization conditions for the preparation of the supports.

Polymer	Oxidant	Oxidant/monomer (mol/mol)	medium	Time
PPy	$FeCl_3.6H_2O$	2.33	Water	6 h
Pani	$K_2S_2O_8$	1.25	HCl 0.2 mol L^{-1}	20 h

Results and Discussion

It was demonstrated that the support alone (PPy or Pani) is able to remove nitrite and nitrate by adsorption and/or direct reduction. The importance of each phenomenon depends on the oxidation state of the polymer. Indeed, when the polymer is totally oxidized, the adsorption of anions is predominant. But when the polymer is partially reduced, it can be oxidized by nitrite or nitrate. Pd/PPy and Pd/Pani are active for nitrite reduction when they are directly used after preparation without activation of the catalyst, thus proving the presence of metallic palladium after the impregnation step. Lastly, bimetallic Pd-Sn catalysts were tested in nitrate reduction. An example of the results is reported in table 2.

Table 2. Catalytic performances of Pd-Sn catalysts supported on Pani, PPy or Al₂O₃

Catalyst	Activity ($\mu mol.min^{-1}.g^{-1}$)	Selectivity in N_2 (%)	Initial pH	Final pH
PdSn/PPy	150	95	3.5	4.8
PdSn/Pani	47	98	2.7	3
PdSn/Al₂O₃	32*	55	5	10

* conversion not completed

The high activity and selectivity obtained in the presence of conducting polymer-supported catalysts are explained by the ability of the support to exchange hydroxide ions formed in the course of nitrate reduction. Indeed, it is well known that the presence of hydroxide, which competes with the adsorption of nitrate on the active metallic phase, leads to a decrease of the activity and selectivity towards nitrogen. For this reason, when classical catalysts are used for nitrate reduction, the pH is maintained at a value lower than 7, by adding an acid in the medium during the reaction. The results presented in table 2 show that, in the presence of the electroactive polymer, able to exchange anions[6], the pH remains stable during the reaction without external pH control. On the contrary, in the presence of the alumina supported catalyst an important increase of the pH is observed explaining the bad performances of this catalyst. The ion exchange property of the polymer depends on its oxidation state which is directly linked to the polymerization conditions and then can be easily modulated.

Significance

Electroactive polymers could be advantageously used as support for noble metal-based catalysts. Indeed, these advanced materials present a wide range of properties (conductivity, acido-basicity, redox behavior, ion-exchange capacity…) which could be interesting for many applications.

References

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