Formation and growth of palladium nanoparticles inside porous poly(4-vinyl-pyridine) monitored by operando techniques: The role of different reducing agents

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ABSTRACT

In this work we followed the formation of palladium nanoparticles, starting from palladium (II) acetate precursor, inside a poly(4-vinylpyridine-co-divinylbenzene) polymer in presence of different reducing agents. The formation and growth of palladium nanoparticles in presence of H_2 was followed as a function of temperature by simultaneous XANES-SAXS techniques, coupled with DRIFT spectroscopy in *operando* conditions. It was found that the pyridyl functional groups in the polymer plays a fundamental role in the stabilization of the palladium (II) acetate precursor, as well as in the stabilization of the palladium nanoparticles. The effect of a thermal treatment in alcohol (ethanol and 2-propanol) was preliminarily investigated by means of DRIFT spectroscopy in *operando* conditions. We found that alcohols act as reducing agents for $Pd(OAc)_2$. The obtained palladium nanoparticles were preliminarily characterized by means of IR spectroscopy using CO as probe molecule.

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1. Introduction

Metal nanoparticles supported on high-surface-area supports are fundamental materials for catalytic applications exhibiting enhanced performances compared to unsupported metal nanoparticles and homogeneous catalysts. In fact, support prevents particles growth and aggregation and allows an easier separation and recovery of the spent catalyst from reaction mixture. Considering the whole branch of heterogeneous catalysts composed of metal nanoparticles, those based on palladium are widely employed in several applications, in combination with various supports having organic (such as carbons) or inorganic (Al_2O_3, SiO_2, and others) nature [1–3]. In particular, palladium nanoparticles supported on porous polymers are a promising class of catalysts showing physical chemical properties different from the most common carbon-based or oxide-based catalysts and attractive catalytic performances [4–13]. For example, polymer-supported palladium-based catalysts have shown remarkable performance in coupling and hydrogenation reactions [14]. The polymer may act simultaneously as support and stabilizer, thanks to the dual effect of porosity (steric stabilization) and polar functional groups (electrostatic stabilization) [15–17]. In polymers without specific functional groups, such as polystyrene-based polymers, stabilization occurs only via electronic interaction between the π electrons of the benzene rings of the polymer and the empty orbitals of metal atoms [11,18,19]. For polymers having specific functional groups, instead, an addi-

tional stabilization mechanism, involving a σ-type coordination between hetero-donor atoms of the functional groups and the surface of metal nanoparticles, may take place. This is an effect similar to what occurs in solution in the presence of classical stabilizers, such as carboxylic acids, thiols, or amines [20]. Highly cross-linked porous polymers with functional groups combine the two stabilization mechanisms, steric and electrostatic (dipole-charge or dipole–dipole interactions).

Recently, we undertook a thorough investigation of palladium-based catalysts supported on highly cross-linked porous polymers with and without functional groups [21–23]. In recent papers [21–23], we proved that the reduction of palladium precursor (palladium(II) acetate), in the presence of H_2 or CO, can be monitored by applying simultaneously Small-Angle X-ray Scattering (SAXS) [24–26] and X-ray Absorption Near Edge Structure (XANES) [27–29] techniques and Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy [30–32] in *operando* conditions. We found that in presence of functional groups, such as the pyridyl group in poly(4-vinylpyridine-co-divinylbenzene), palladium (II) acetate is stabilized through the coordination of Pd^{2+} cations, with the consequent rupture of the trimeric structure characteristic for solid palladium (II) acetate, and the restructuring of the acetate ligands in a monodentate coordination. In addition, extremely small (<2 nm) and very homogeneous palladium nanoparticles are formed upon H_2 reduction [21], compared to those obtained in polymers without functional groups, such as poly(ethylstyrene-co-divinylbenzene).

Herein we extend our previous study to investigate the behavior of palladium (II) acetate inside the same poly(4-vinylpyridine-co-divinylbenzene) matrix, but in presence of alcohols as reducing agents. Indeed, palladium-catalyzed reactions (e.g. hydrogenation, Suzuki-Miyaura Cross-Coupling reaction, and others) [33] are often conducted in slurry conditions, using alcohols as solvents, because alcohols combine good solvation properties for organic compounds with a low price. Hence, understanding the role of alcohols in palladium-catalyzed reactions is of prime interest in the optimization of the reaction variables.

In other cases, alcohols are used as reactants. For example, alcohol hydrogenation, oxidation and cross-coupling reactions are also catalyzed by palladium-based catalysts, either homogeneous or heterogeneous [34–41]. In this respect, the homogeneous $Pd(OAc)_2$/pyridine system is by far one of the most efficient and selective catalyst for oxidation of alcohols to aldehydes. The reaction mechanism has been proposed by Stahl and coworkers [38–40] as an oxidase-style mechanism in which palladium(II)-mediated substrate oxidation (Stage I in Scheme 1) and aerobic oxidation of the catalyst (Stage II in Scheme 1) occur in two independent, sequential stages. Formally, in Stage I Pd(II) species transform into Pd^0 ones, while in the Stage II oxidation by oxygen restores the Pd(II) original complex. These steps occur with the contemporary elimination (Stage I) or addition (Stage II) of acetic ligands. The main cause of deactivation for the homogeneous $Pd(OAc)_2$/pyridine catalyst is the formation of metal nanoparticles, which occurs when Stage II is inhibited, that is in absence of oxygen.

In our prospect, the palladium (II) acetate inside the porous poly(4-vinylpyridine-co-divinylbenzene) matrix may show catalytic behavior similar to the $Pd(OAc)_2$/pyridine system, provided that the reaction conditions (reagents mixture, temperature, etc.) are properly set. To this aim it is important to understand the effect of alcohols on P4VP/$Pd(OAc)_2$, in absence and in presence of oxygen, as a function of the reaction temperature. The present paper deals with the first step (understanding the role of alcohols in absence of oxygen), while the second step will be the subject of a successive work. Since alcohols are mild reducing agents, the redox behavior of palladium (II) acetate inside poly(4-vinylpyridine-co-divinylbenzene) in presence of H_2 as a function of temperature
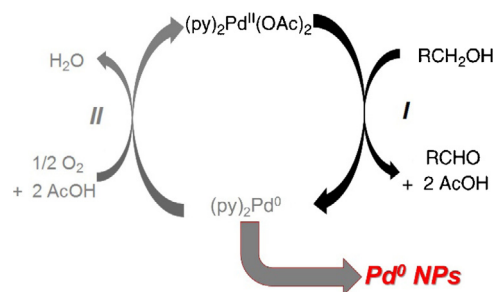
Scheme 1. Catalytic cycle for alcohol aerobic oxidation catalyzed by homogeneous $Pd(OAc)_2$/Pyridine catalyst as proposed by Stahl et al. [38–40]. Stage I (black arrows) involves alcohol oxidation into aldehyde/ketone by eliminating acetate ions as acetic acid; Stage II (grey arrows) involves the active species regeneration, by converting acetic acid and O_2 into acetate ions and water. The absence or the loss of efficiency of Stage II, results in the formation of precipitated Pd^0 nanoparticles, causing the deactivation of the catalyst in the homogeneous phase.

is discussed first. In particular, we summarize our recent results obtained by applying: (i) simultaneous XANES-SAXS techniques, which give direct information on the oxidation state and electronic density of the palladium phase; (ii) operando DRIFT spectroscopy, which gives information on the acetate ligands; and (iii) IR spectroscopy of adsorbed CO, which provides information on the surface properties of palladium nanoparticles. In the second part of the paper we present DRIFT data in operando on the effects of different alcohols (ethanol and 2-propanol) on the same system as a function of temperature.

2. Sample and Methods

2.1. Investigated catalyst

The starting catalyst was obtained by impregnating a commercial poly(4-vinylpyridine-co-divinylbenzene) polymer (P4VP hereafter), commercialized by Sigma Aldrich, with a solution of palladium (II) acetate ($Pd(OAc)_2$ hereafter) in acetonitrile, having a final palladium loading of 5 wt.%. The polymeric support has a specific surface area of about $50 \, m^2 \, g^{-1}$, which is relatively poor compared to other supports [21]. However the presence of the pyridyl group plays a fundamental role in the dispersion and in the stabilization of the palladium precursor. After impregnation, the sample was dried at room temperature. Finally, the sample was gently grinded in a mortar in order to obtain a powder.

2.2. Experimental methods

FT–IR spectra were collected in diffuse reflectance mode (DRIFT) on a Nicolet 6700 instrument, equipped with a MCT detector, using a Thermo Fisher Environmental Chamber to record data under reaction conditions. FT-IR spectra were recorded at regular temperature intervals during the whole reaction at a spectral resolution of $4 \, cm^{-1}$, averaging 64 spectra. Thermal treatments in presence of H_2 or alcohols were performed following a temperature ramp of $2 \, °C \, min^{-1}$, from $25 \, °C$ up to $200 \, °C$. The cell was connected to a gas-flow system (under atmospheric pressure), equipped with Brooks Instrument Delta Smart Mass Flow Controllers (MFC), controlled via Read Out & Control Electronics 0154 by Brooks Instrument. The MFCs were calibrated for each gas used using Agilent Optiflow 570 instrument. A total flow of $25 \, ml \, min^{-1}$ was used. Reduction was performed either in H_2 (5% H_2 in N_2), or in presence of alcohols (ethanol and 2-propanol). In the latter cases, vapors of alcohols were dosed from the liquids at room temperature, exploiting a $25 \, ml \, min^{-1} \, N_2$ stream. After the reduction step, the sample was cooled at room temperature in inert atmosphere. Successively, 50%