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Kinetic analysis of reduction of 4-Nitrophenol by (water soluble) Palladium Nanoparticles Studied by a Langmuir-Hinshelwood mechanism. Does we compare apples and oranges ?

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PURPOSE OF THE ABSTRACT

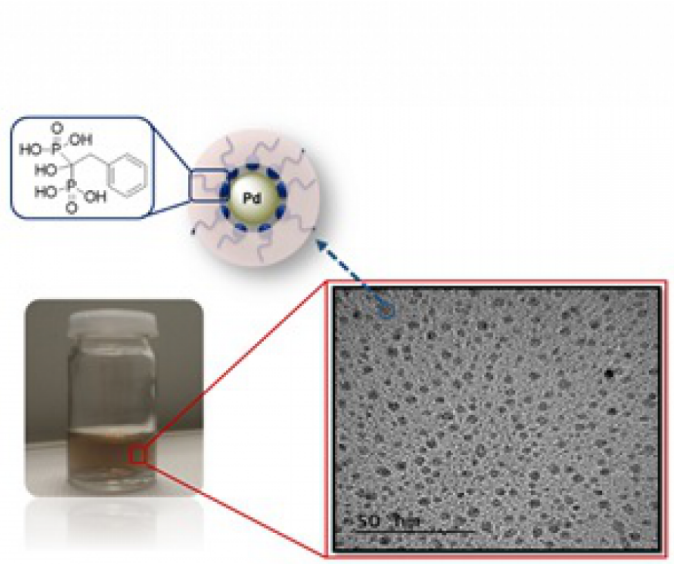
Aromatic nitro molecules are significant side product obtained from pharmaceutical industries, synthetic dyes, herbicides, and pesticides. In particular, nitrophenol are harmful industrial pollutants and environmentally hazardous organic compounds with high solubility and stability in water. Additionally, they are known as hazardous molecules that can cause damage to the human and animal blood, organs like kidney, central nervous system, liver, etc [2]-[4]. Therefore, their removal from the environment is an essential duty and several catalyzed protocols have been studied recently for their reduction in less hazardous aromatic amine. In the quest for eco-friendly development, important attention has been paid to the use of nanoparticles in aromatic nitro reduction, due to their unique properties and their enhanced surface volume ratio putting them at the frontier between heterogeneous and homogeneous catalysis [5,6]. Therefore, in the past few years, 4-nitrophenol reduction by sodium borohydride has become the benchmark reaction to compare metallic nanoparticle based catalysts [1], [7], [8] [9]. It is now qualified as a model reaction to be used to study the full kinetics of catalysis by metallic nanoparticles. This is because reaction is well-controlled without by-products, and the kinetic analysis of the reaction rate as a function of temperature is monitored by UV-vis spectroscopy with high accuracy. In addition, this reaction proceeds under mild conditions (at room temperature in water as solvents). Almost all authors consider that the catalysis reduction of 4-nitrophenol takes place on the surface of the Metal nanoparticles [2], [10]. The apparent rate constant kapp is determined based in terms of a Langmuir-Hinshelwood kinetics, which prerequisite that all reactants, 4-nitrophenol and borohydride ion must be adsorbed on the surface of Metal nanoparticle to react.

In this context, we proposed to study this headmost model catalytic reactions to test the catalytic activity of our Pd nanoparticles dispersed in (water) as a catalyst. We assumed that all steps of this reaction proceed only on the surface of Pd nanoparticles (Langmuir-Hinshelwood model). A schematic representation of the Langmuir-Hinshelwood mechanism of 4-Nip reduction on the surface of Pd nanoparticles is presented. We reports

the effects of different initial 4-nitrophenol and sodium borohydride concentrations, reaction temperatures, and quantity of Pd nanoparticles on catalytic reduction kinetic. The whole kinetics of the reduction process has been studied by varying a single factor each time at various conditions, as the amount of nanocatalyst, initial 4-nitrophenol and NaBH4 concentration. The true rate constants (k), and the adsorption constants (K4-Nip and KBH4), as well as the thermodynamic parameters (activation energy, enthalpy, and entropy), were determined at different temperatures by fitting the experimental data with Langmuir-Hinshelwood model.

Our results show that to compare the different catalysts thus the apparent constant Kapp, it is necessary to work under certain conditions in a 4-Nip concentration zone with a NaBH4 ratio that need to be strictly set so that apparent constant Kapp is constant and the comparison valid. We, therefore, highlight that in contrast to what is reported in the literature great care is to be given to the experimental conditions in which the catalytic reduction is performed to be able to compare efficiently metallic nanoparticle based catalyst otherwise it will be as comparing apple to oranges.

FIGURES



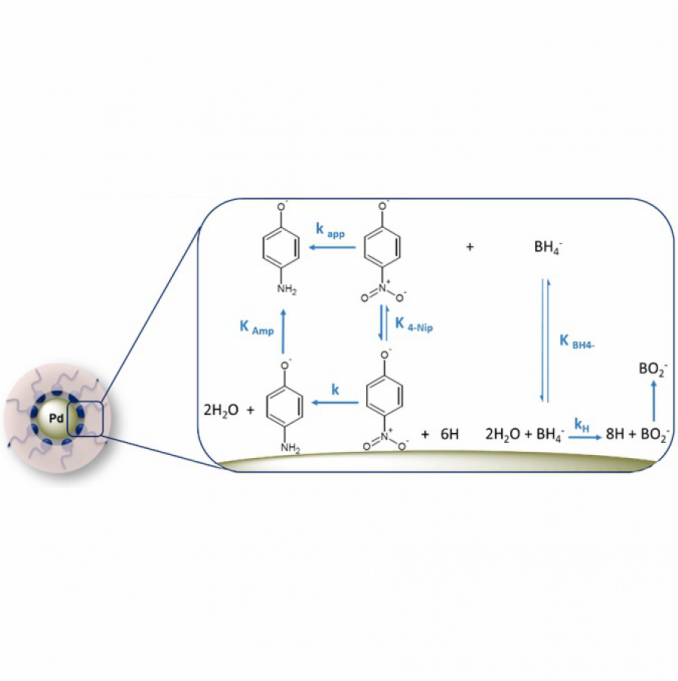


FIGURE 1

Structure of the Pd NPs used in the kinetic studies.

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FIGURE 2

A schematic representation of the Langmuir-Hinshelwood mechanism of 4-Nip reduction on the surface of Pd nanoparticles.

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KEYWORDS

Nanoscience | Green Chemistry | 4-nitrophenol reduction | Langmuir-Hinshelwood Model

BIBLIOGRAPHY

[1] N. Pradhan, Colloids Surfaces A Physicochem , 2002 Eng. Asp., vol. 196, no. 2–3, pp. 247–257.

[2] N. C. Antonels, Langmuir, vol. 29, pp. 13433–13442, 2013.

[3] J. Chen, Environ. Toxicol. Pharmacol., vol. 41, pp. 266–271, 2016.

[4] K. B. Narayanan, J. Hazard. Mater, vol. 189, no. 1–2, pp. 519–525, 2011.

[5]. Astruc D, Lu F, Aranzaes JR. Angew Chem Int Ed 2005 ; 44:7852e72.

[6]. Rangheard, C., 2010, Dalton Transactions. 39, 36, p. 8464-8471 8 p.

[7] S. Wunder, ACS Catal., vol. 1, pp. 908–916, 2011.

[8] S. Wunder, J. Phys. Chem. C, vol. 114, no. 19, pp. 8814–8820, 2010.

[9] P. Hervés, Chem. Soc. Rev., vol. 41, no. 17, pp. 5577–5587, 2012.

[10] M. A. Mahmoud, J. Phys. Chem. C, vol. 117, no. 42, pp. 21886–21893, 2013.