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Unexpected ligand effect on the catalytic reaction rate acceleration for hydrogen production using biomimetic nickel electrocatalysts with 1,5-diaza-3,7-diphosphacyclooctanes

Vera V. Khrizanforova [a, *], Elvira I. Musina [a], Mikhail N. Khrizanforov [a],
Tatiana P. Gerasimova [a], Sergey A. Katsyuba [a], Yulia S. Spiridonova [a], Daut R. Islamov [b],
Olga N. Kataeva [b], Andrey A. Karasik [a], Oleg G. Sinyashin [a], Yulia H. Budnikova [a]

[a] A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of Russian Academy of Sciences, 8, Arbuzov str., 420088 Kazan, Russian Federation
[b] Kazan Federal University, 18, Kremlevskaya str., 420008 Kazan, Russian Federation

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ABSTRACT

The two new nickel complexes $[Ni(P^R_2N^{Ph(CH)Ph}_2)_2]^{2+}$ (where R = Ph or o-Py) with cyclic 1,5-diaza-3,7-diphosphacyclooctane ligands have been synthesized. All complexes are effective electrocatalysts for hydrogen production using $[(DMF)H]^+$ as proton source in acetonitrile. The bulky benzhydryl substituent at nitrogen atom leads to higher catalytic activity comparison to benzyl. The introduction o-Py substituents at phosphorus as additional basic center is caused by the changing of voltage—current picture and significantly catalytic current enhancement. TOFs being 100 and 15200 s^{-1} for R = Ph and o-Py, respectively.

Introduction

The development of renewables is important for the future of the energy frontiers, partly because of mitigating increasing CO_2 concentrations in the atmosphere resulting from the burning of mineral fuels [1]. One of the simplest reactions for storage of renewable energy is the formation of H_2 from two protons and two electrons. Platinum and the hydrogenase enzymes are excellent catalysts for both production and oxidation of hydrogen.

Platinum, however, is a precious metal with high cost and low abundance [2]. Hydrogenase enzymes being remarkably efficient catalysts in nature [3—5], are expensive to be obtained commercially, unstable and difficult to adapt to large-scale commercial applications. These considerations have motivated efforts to design molecular catalysts that employ more abundant metals, such as nickel [6—11], cobalt [12—20], iron [21—34], or molybdenum

[35—37], as electrochemical catalysts for the production and oxidation of dihydrogen [38,39].

The [FeFe]-hydrogenase enzyme can both produce and oxidize H_2 at turnover frequencies of ≥ 9000 s^{-1} [3,4,40,41]. Recent advances in Ni-based bio-inspired catalysts [6—11], such as $[Ni(P^R_2N^{R'}_2)_2]^{2+}$, demonstrated the possibility of cleaving H_2 or generating H_2 heterolytically with turnover frequencies comparable or superior to those of hydrogenase enzymes. In these catalysts the transformation between H_2 and protons proceeds via an interplay between proton, hydride and electron transfer steps, and involves the interaction of a dihydrogen molecule with both a Ni(II) center and pendent amine bases incorporated in six-, seven or octa-membered rings, which function as proton relays. The catalysts with ligand 8-membered ring achieved the high electrocatalytic H_2 production rates, up to 1540 s^{-1} in dry acetonitrile and up to 6700 s^{-1} in water-acetonitrile solutions with [(DMF)H]OTf acid [42—45] as proton source.

In this communication we report new data on the unexpectedly high activity of nickel complexes with 8-membered ring 1,5-diaza-3,7-diphosphacyclooctane ligands with the diphenylmethyl

* Corresponding author. Tel.: +7 (843)279 53 35; fax: +7 (843)275 22 53.
E-mail address: KhrizanforovaVera@yandex.ru (V.V. Khrizanforova).