Supplementary Material

Niobic Acid as Support for Microheterogeneous Nanocatalysis of Sodium Borohydride Hydrolysis Under Mild Conditions

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1. Determination of the amount of hydrogen gas released

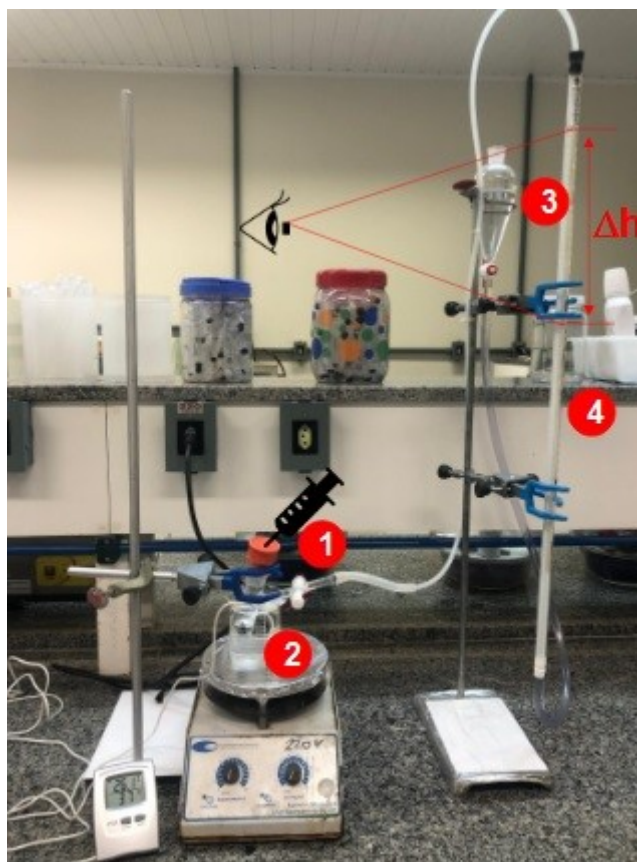The hydrogen production system utilized during the experiments can be seen in Fig. S1.

Fig. S1- Hydrogen production system. (1) NaBH$_4$ solution injection; (2) Temperature control and agitation; (3) Separation funnel containing water; (3) Burette filled with water.

The hydrogen gas released during the reaction diffuses through the system, leading to an increase in its pressure. To establish equilibrium between the internal pressure of the system and the external pressure, a water displacement occurs in the burette. This displacement was captured on video to provide the necessary data for subsequent calculations. At each moment, the hydrogen pressure reaches equilibrium with the atmospheric pressure (since the system is open), in addition to the hydrostatic pressure (Eq.

S1). Other forces (such as the adhesion of water to the walls of the burette) were considered negligible in this context.

$$P_{H_2} = P_{atm} + \rho g \Delta h \text{ (Eq.S1)}$$

where:

P_{H_2} is the hydrogen pressure (Pa);

P_{atm} is the atmospheric pressure (Pa);

ρ is the density of water in the burette (kg m^{-3});

g is the acceleration of gravity at Viçosa, state of Minas Gerais, Brazil (9.78 m s^{-2})[1];

Δh is the water displacement in the burette (m).

Given that the reactions took place at room temperature and under low pressures, and taking into account the weak intermolecular forces exhibited by hydrogen gas, the ideal gas law can be employed to describe the behavior of the gas and then calculate the amount of hydrogen gas released (Eq. S2):

$$n_{H_2} = \frac{P_{H_2} V_{H_2}}{RT} \text{ (Eq. S2)}$$

where:

P_{H_2} is the hydrogen pressure in Pa;

V_{H_2} is the volume of hydrogen released (m^3);

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[1] This value was calculated by the Department of Physics of Universidade Federal de Viçosa and is used in experimental classes.

n_{H_2} is the amount of hydrogen released (mol);

R is the universal gas constant (8.314 J mol^{-1} K^{-1});

T is the reaction's temperature (K).

The atmospheric pressures for each experiment were extracted from the data provided by the meteorological station in Viçosa[2], state of Minas Gerais, Brazil, while the water density in the burette was calculated according to Wolfram Alpha® Water Calculator Widget[3].

2. Raman spectrum for niobic acid

The Raman spectrum of niobic acid is shown in Figure S2, revealing three distinct band regions. The first one, observed at 637 cm^{-1}, can be attributed to the Nb-O-Nb vibrations. A second, weaker band, at 817 cm^{-1}, can be identified as the symmetric stretching mode of Nb-O on the material's surface. Additionally, bands around 180 cm^{-1} can be assigned to the Nb-O-Nb bending modes (Stošić *et al*., 2014). It is also worth noting the broad bands in the spectrum of the materials treated at lower temperatures, characteristic of amorphous materials (Stošić *et al*., 2014).[4]

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[2] Universidade Federal de Viçosa – UFV. Departamento de Engenharia Agrícola. Estação Climatológica Principal de Viçosa. **Boletim meteorológico 2023**. Viçosa, MG: UFV, 2023.
[3] https://www.wolframalpha.com/widgets/view.jsp?id=1de7d2b90d554be9f0db1c338e80197d
[4] Stošić D, Bennici S, Pavlović V, et al (2014) Tuning the acidity of niobia: Characterization and catalytic activity of Nb2O5-MeO2 (Me = Ti, Zr, Ce) mesoporous mixed oxides. Mater Chem Phys 146:337–345. https://doi.org/10.1016/j.matchemphys.2014.03.033
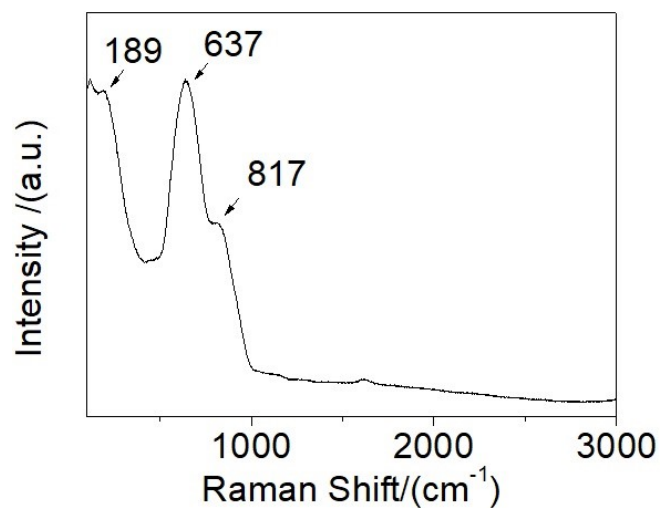
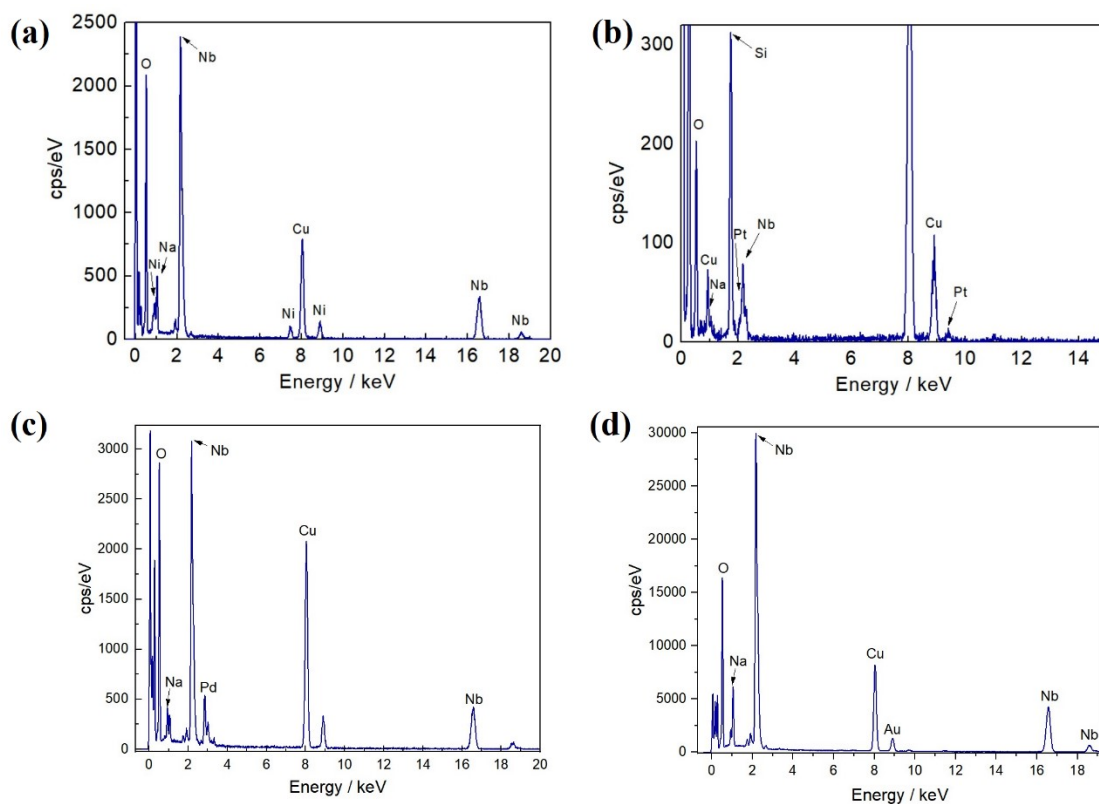**Fig. S2** -Raman spectrum of niobic acid.

3. EDS spectra

Fig. S3- EDS spectra for NiNPs (a), PtNPs (b), AuNPs (c), and PdNPs (d) deposited on niobic acid. The peaks corresponding to C and Cu are from the equipment and the sample preparation.

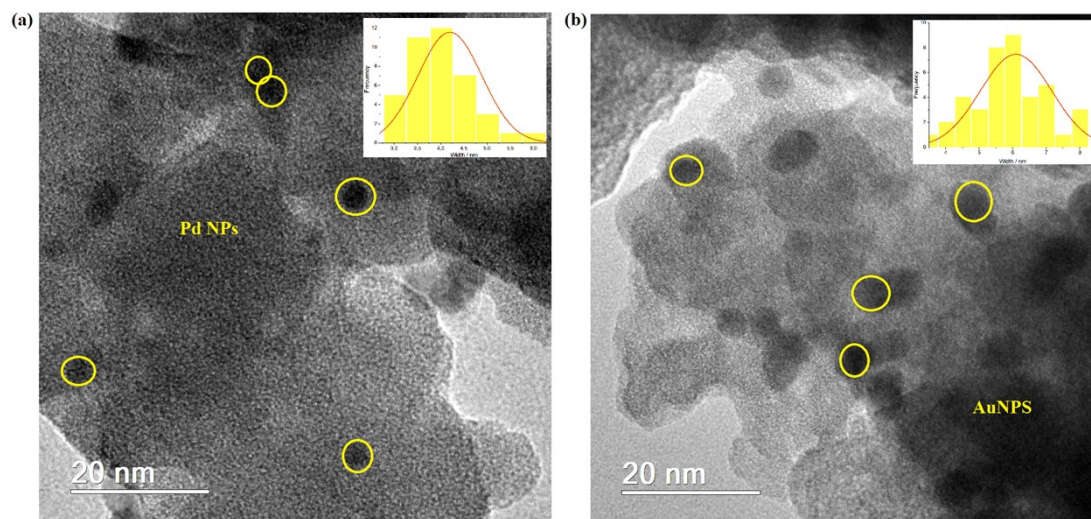# 4. Transmission Electron Microscope (TEM) for PdNPs/Nb$_2$O$_5$.nH$_2$O and AuNPs/Nb$_2$O$_5$.nH$_2$O

Fig. S4 – Transmission Electron Microscope (TEM) images for (a) PdNPs/Nb$_2$O$_5$.nH$_2$O, inset: PdNPs size distribution. and (b) AuNPs/Nb$_2$O$_5$.nH$_2$O, inset: AuNPs size distribution.

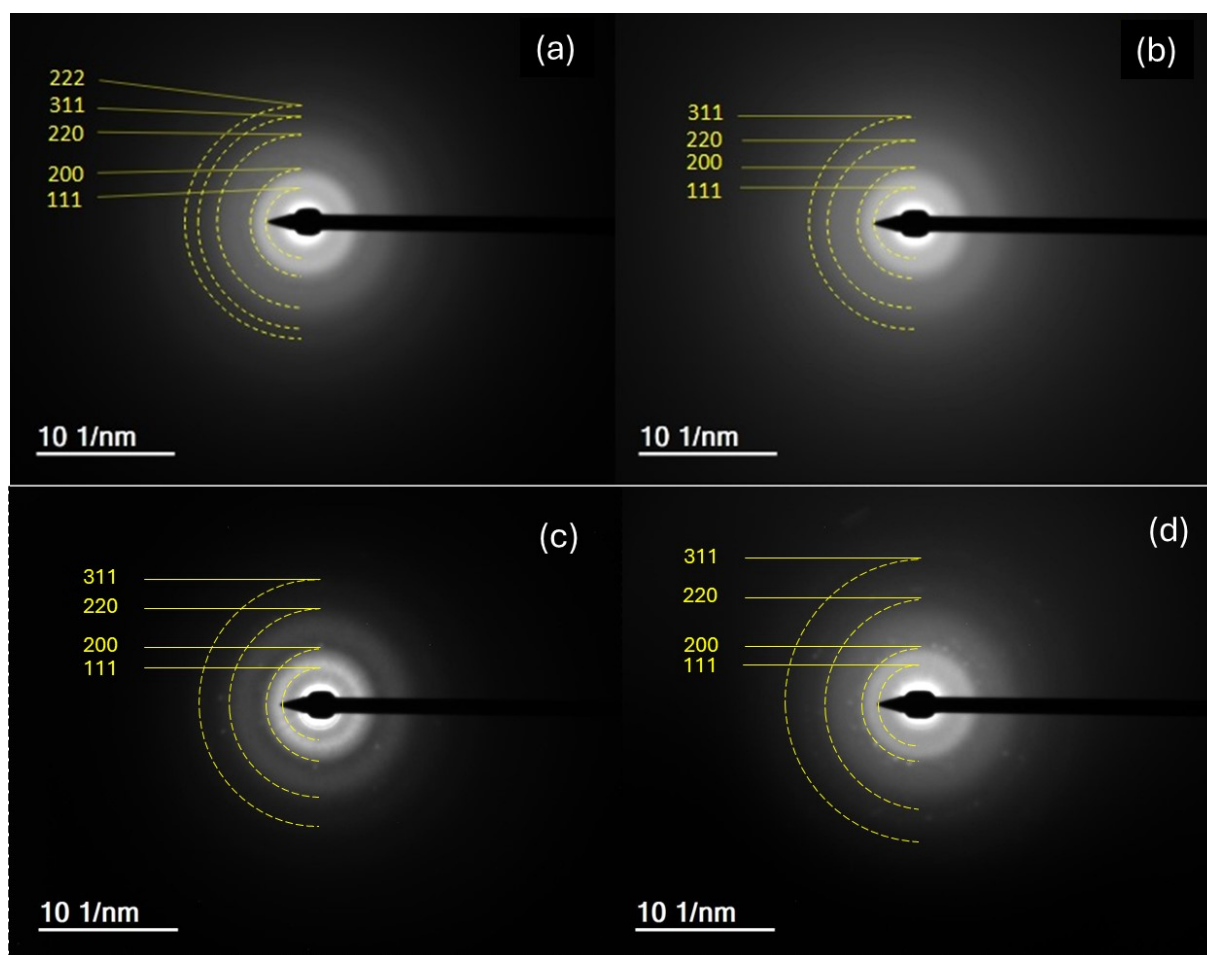## 5. Selected area electron diffraction (SAED)

Fig. S5- SAED Pattern of (a) NiNPs deposited on niobic acid, (b) PtNPs nanoparticles deposited on niobic acid, (c) PdNPs nanoparticles deposited on niobic acid and (d) AuNPs nanoparticles deposited on niobic acid.

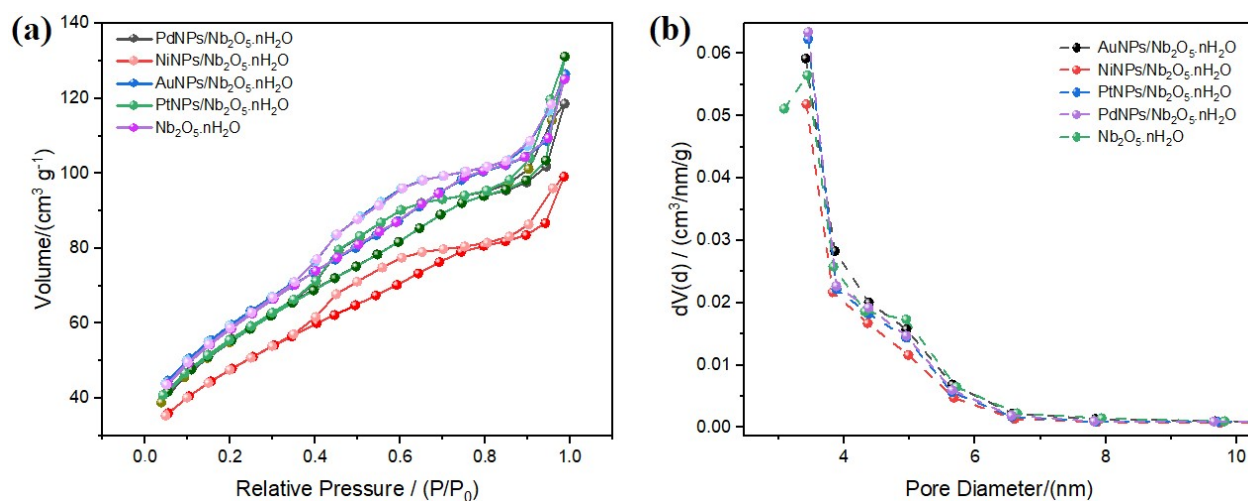## 6. Surface Area Analysis and Pore Size Distribution for NPs/$Nb_2O_5.nH_2O$

Fig. S6- Surface Area Analysis (BET) and Pore Size Distribution (BJH) of NPs/$Nb_2O_5.nH_2O$.

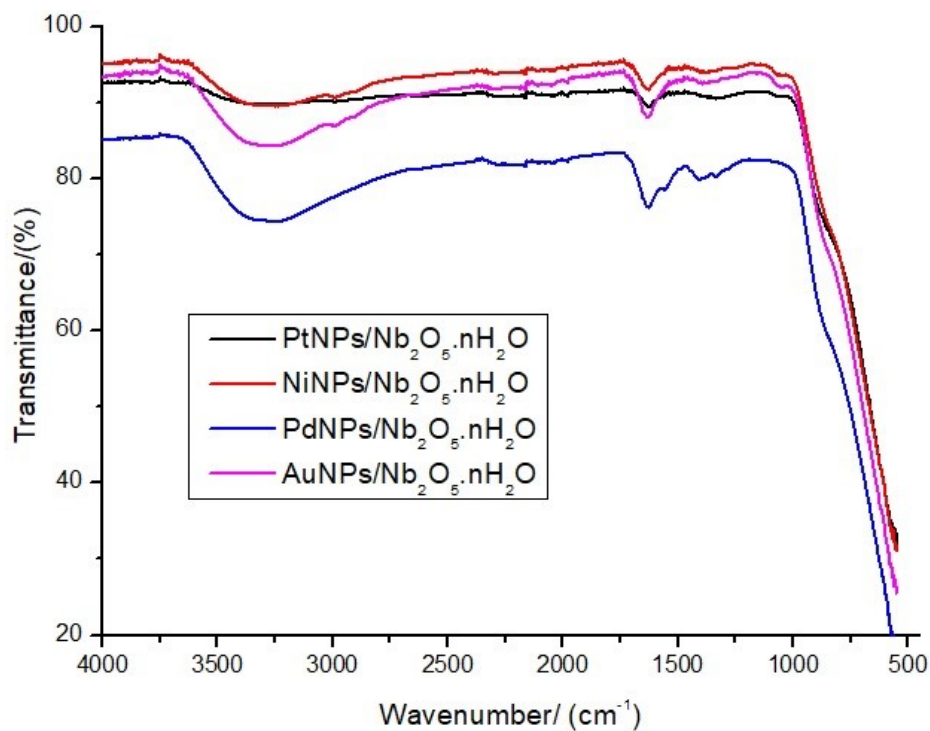## 7. ATR-FTIR spectra of NPs/Nb$_2$O$_5$.nH$_2$O

Fig. S7- ATR-FTIR spectra for AuNPs, PdNPs, PtNPs, and NiNPs deposited on Nb$_2$O$_5$.nH$_2$O.

8. Determination of the kinetic parameters

To obtain the kinetic parameters, the general equation Eq. S3 was utilized:

$$\frac{dC}{dt} = - kC^n \quad \text{(Eq. S3)}$$

where:

C represents the concentration of sodium borohydride in solution (mmol L^{-1})[5];

t is the time (s);

k is the kinetic constant at a given temperature, and

n denotes the order of the reaction.

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[5] Sodium borohydride concentration was calculated based on the stoichiometric coefficients of Eq. 1: for each 1 mol of sodium borohydride consumed, 4 mol of hydrogen gas are released.

It is important to note that although water participates in the reaction (Eq.1), its concentration remains essentially constant due to its excess. Since the catalyst dose was not changed, it is also considered constant. The differential equation described in Eq. S3 can be solved using the separation of variables method (Eq. S4), resulting in two distinct solutions described by Eq. S5 and Eq. S6:

$$\int_{C_0}^{C} \frac{dC}{C^n} = -k \int_{0}^{t} dt \qquad \text{(Eq. S4)}$$

where "C_0" represents the initial concentration of sodium borohydride and "k" is considered constant at a constant temperature.

If $n=1$, then:

$$\ln\frac{C}{C_0} = -kt \qquad \text{(Eq. S5)}$$

And if $n \neq 1$, then:

$$\frac{C^{1-n} - C_0^{1-n}}{1-n} = -kt \qquad \text{(Eq. S6)}$$

Assuming that the left-hand sides in Eq. S5 and Eq. S6 can be generalized as F(C), referred to as the "test function", both equations give rise to a linear equation, shown in Eq. S7:

$$F(C) = -kt \qquad \text{(Eq. S7)}$$

To determine the most suitable value of "n" (order of the reaction) that best fits Eq. S5-S6, the "Goal seek" function (Tools → Goal seek) on LibreOffice Calc (version 7.4.7.2) was employed.

To obtain the correlation of the data according to Eq. S7, "time x sodium borohydride concentration" data were inserted on LibreOffice Calc's spreadsheet (Figure S5). Then, the F(C) value was calculated using the command described by Eq. S8:

$$\text{=IF(\$F\$5=1,LN(B3/\$B\$3),(((B3\textasciicircum(1-\$F\$5))-(\$B\$3\textasciicircum(1-\$F\$5)))/(1-\$F\$5)))} \text{ (Eq. S8)}$$

Using an iterative method provided by the "Goal seek" function, "n" (F5 cell in Fig. S5) was varied until the determination coefficient of the linear regression of the data set "time x F(C)" approached closest to 1 (F7 cell in Fig. S5). The module of the slope of the linear equation obtained corresponds to the rate constant "k" (F6 cell in Fig. S5).

Fig. S8- Example of the spreadsheet utilized to calculate the kinetic parameters for sodium borohydride hydrolysis. LibreOffice Calc version 7.4.7.2.

9. Remarks on the temperature increase in the reaction medium

Given that reaction rates are sensitive to changes in temperature, we wanted to estimate the potential temperature fluctuations in the reaction system under a worst-case scenario. In this scenario, we assumed there would be no temperature control measures in place, such as water or oil baths. It is important to address this issue because, for a fast reaction with a small amount of solvent, there will likely not be enough time for the heat to transfer from the reaction mixture to the walls of the flask and, from the walls of the flask to the bath.

According to Zhang et al. (2006), sodium borohydride hydrolysis is exothermic and releases *c.a.* 210 kJ mol^{-1} of energy. As for the reactions performed in this work, 0.5 mmol of sodium borohydride was used, which would result in a release of *c.a.* 105 J. Considering the yield of the reactions, a rough estimation would involve assuming a 70% conversion, resulting in a release of only 73.5 J of energy. The heat transfer equation is given in Eq. S9:

$$Q=mc\Delta T \text{ (Eq. S9)}$$

where:

Q is the amount of heat released in sodium borohydride hydrolysis;

m is the water's mass;

c is the specific heat for water (considered constant and equal to 4.184 J g^{-1} °C^{-1});

ΔT is the variation of temperature.

Assuming that the solids present in the reaction do not interfere with the heat transfer (given their significantly lower quantities) and that the water's density is 1.0 g mL^{-1}, applying Eq. S9 results in $\Delta T = + 0.8$ °C, for the reaction in 21 mL of water, and $\Delta T = + 8.8$ °C, for the reaction in 2 mL of water. While the difference in temperature for the former reaction might

be considered negligible, the difference in temperature for the latter one may interfere with the rate's constant, assuming "k" being constant throughout the reaction more difficult to uphold. Again, this would be a worst-case scenario but, even if that was the case, for the sake of simplicity, it is plausible to keep the approach described in section 4 of this Supplementary material, even when only 2 mL of solvent were used is used in the experiments with deuterated water. Both reactions were performed at the same conditions except for the change in the solvent. Although the change in temperature in deuterated water is lower due to its higher specific heat, such a difference can be easily considered negligible, since the specific heat of deuterated water at 22 °C is only 0.6 % higher than that of water itself[6]. That being said, changes in temperature for both reactions would cancel out in a way that any differences in kinetics may be indeed attributed solely to the presence of a primary isotope effect.

10. Reagent cost

Table S1 - Reagent cost.

Reagent	Reagent cost	Cost of the 34.45 µmol of metal used in the synthesis
$H_2PtCl_6 \cdot 6H_2O$	US\$ 172/ 1g	US\$ 3.07
$NiSO_4 \cdot 6H_2O$	US\$ 169/ 500 g	US\$ 0.01
$HAuCl_4.3H_2O$	US\$ 173/ 1g	US\$ 2.35
K_2PdCl_4	US\$ 159/ 2g	US\$ 0.89

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[6] Cockett, A. H., & Ferguson, A. (1940). XXI. The specific heat of water and of heavy water. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 29(193), 185–199. doi:10.1080/14786444008521257 .