

CATALYTIC ACTIVITY OF THE NOBLE METAL NANOPARTICLES

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Abstract

Noble metal nanoparticles are excellent catalysts for many industrial important reactions. Because heterogenous catalysis is dependent strongly on the surface of catalyst the nanomaterials are better catalysts in comparison with the bulk materials. However, it is important for optimization of the effectivity of catalytic process to have a comparison of the nanostructured catalysts of different nature for application in the particular reaction. As a model for this process was conducted primary testing of catalytic activity of five noble metal nanoparticles (Ru, Rh, Os, Ir, Pt) in redox reaction (reduction of 4-nitrophenol by the borohydride). It is interesting that for this model reaction the best catalyst is rhodium with the shortest induction period and fastest main part of the reaction course. On the other hand, platinum nanoparticles are not the best catalyst for the studied model reaction.

Keywords: Nanoparticles, noble metals, catalytic activity, model reaction, 4-nitrophenol

1. INTRODUCTION

Nanoparticles of metals, especially noble metals from the platinum group, show high catalytic activity with high potential for use in practical applications. Typically, these materials are tested as suitable catalysts for fuel cells [1]. These catalytic metals are currently difficult to replace in the redox reactions [2], but a similar situation prevails in the field of other types of catalytic reactions. Hydrogenations of unsaturated hydrocarbons can be mentioned as reaction mostly applicated in practice [3]. However, the catalytic action of this type of nanoparticles is also studied in other types of reactions - preparation of hydrogen by hydrolysis of ammonium borane [4] or in catalytic oxidation of organic compounds [5]. These metal nanocatalysts are frequently studied in reactions useful in environmental technologies [6]. In this respect, they are involved in a number of studies where a model reaction is used to assess their basic catalytic activity. Typically, the most used model reaction is reduction of 4-nitrophenol to 4-aminophenol. [7].

Preparation of nanoparticles of these noble metals is most easily accomplished by the method of chemical reduction of a salt of a given metal using a suitable reducing agent. When NaBH₄ is used as a reducing agent, the smallest particles in the range of about 1.5-5 nm are formed for all metals in this group [1,8]. However, since the metal nanoparticles prepared by this method easily aggregate, they are stabilized using protective layers formed by surfactants [9] or polymers [7,10]. Stabilization can be also realized by anchoring of nanoparticles on the surface of a solid inert substrate of the type of carbonaceous materials [3] or inorganic substances such as ZnO [11]. On the other way, the reducing action of weak reducing agents, as are polyols, are often used in this field [2,12]. Due to the highly positive redox potential of noble metal ions, the so-called "green synthesis", which has recently become very popular, using natural substances as reducing agents and stabilizers of the resulting nanoparticles, can also be used in the preparation of this type of nanoparticles. Thus, for example, Pd nanoparticles can be prepared by reduction with polyphenols from black tea extract. [13]

However, very few studies can be found in the available literature offering a basic comparison of the catalytic activity of platinum metal nanoparticles prepared by the same method in the same standard reaction. Therefore, this study is aimed at platinum metal nanoparticles which were prepared using reduction synthesis with NaBH_4 and then they were tested for their catalytic activity in the most commonly used model reaction - reduction of 4-nitrophenol with NaBH_4 .

2. EXPERIMENTAL

2.1. Chemicals

The chemicals that were used for the preparation of nanoparticles and subsequent kinetic experiments are listed in **Table 1**. Deionized water ($18 \text{ M}\Omega \cdot \text{cm}$, Millipore) was used to prepare all solutions.

Table 1 Chemicals for nanoparticle preparation and kinetics experiments

Formulae	Name	Producer	Molar weight (g/mol)
NaBH_4	Sodium borohydride	Sigma-Aldrich	37.83
$\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$	Trisodium citrate dihydrate	Lach-Ner	294.1
$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$	Ruthenium(III) chloride hydrate	Merck KGaA	207.43
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	Rhodium(III) chloride trihydrate	Merck KGaA	263.32
PdCl_2	Palladium(II) chloride anhydr.	Sigma-Aldrich	177.33
$\text{OsCl}_3 \cdot x\text{H}_2\text{O}$	Osmium(III) chloride hydrate	Sigma-Aldrich	296.59
$\text{IrCl}_3 \cdot x\text{H}_2\text{O}$	Iridium(III) chloride hydrate	Merck KGaA	298.58
PtCl_4	Platinum(IV) chloride	Merck KGaA	336.89
$\text{C}_6\text{H}_5\text{NO}_3$	4-nitrophenol	Lachema	139.11

2.2. Nanoparticles preparation

Nanoparticles of all metals used in this study were prepared in the same way - reduction of a salt of a given metal with borohydride and citrate. Citrate also serves as a stabilizer of the resulting nanoparticles. The reaction takes place at room temperature. In a 50 ml beaker, mix 5 ml of NaBH_4 solution with a concentration of $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ and 5 ml of sodium citrate solution with a concentration of $2 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ while stirring. To the solution is then added water to obtain total volume 20 ml and then left to stand for about 20 minutes. Subsequently, 5 ml of a $4.96 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ salt solution of the metal are added dropwise. The reaction is stopped after stirring for another about 20 minutes.

2.3. Nanoparticles characterization

The resulting colloidal dispersions were characterized by UV-Vis spectroscopy and the dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern Instruments, UK) method. However, the particle sizes measured by DLS were taken as indicative only, and the actual particle size was determined only from transmission electron microscope images (TEM, JEM 2100, Jeol Ltd., Japan). UV-Vis spectra (Specord S600, Analytic Jena AG, Germany) were obtained after 10-fold dilution of resulting dispersions.

2.4. Catalytic experiments

For the purpose of evaluating the catalytic activity of the prepared nanoparticles, a solution of 4-nitrophenol with a concentration of $1.5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ was prepared, which was used in all experiments. The NaBH_4 solution ($8 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) was prepared fresh before each experiment due to its considerable instability. The reaction system was prepared by mixing 0.03 ml of the prepared nanoparticle dispersion, 0.09 ml of 4-nitrophenol (4-NP) solution and 1.28 ml of water. A cuvette with this solution was placed in a UV-Vis spectrophotometer (Specord S600, Analytic Jena AG, Germany), the measurement being started immediately after the addition of 1.6 ml of NaBH_4 solution. The NaBH_4 solution must be allowed to stand for 20 minutes after preparation so that the kinetic experiment takes place at a time when its reducing power is the best. All measurements were performed in a quartz cuvette in the wavelength range of 250-600 nm. The duration of the experiment was set to 20 minutes, measured every 10 seconds.

3. RESULTS AND DISCUSSION

3.1. Nanoparticles preparation

Noble metal nanoparticles prepared by the above reduction method were characterized by UV-vis spectroscopy and their size was evaluated from TEM images (**Figure 1**). The one same procedure was used to prepare nanoparticles of all platinum metals with the exception of palladium, whose nanoparticles in the given method of preparation quickly aggregated and the resulting aggregates sedimented to the bottom of the reaction vessel. Because the aim of this study was to evaluate the catalytic activity of unmodified metal nanoparticles, no attempt was made to stabilize these nanoparticles with surfactants or polymers that can fundamentally affect the resulting catalytic activity [14]. In all cases, a strong absorption peak in the region of 190-210 nm appeared in the UV-vis spectra (**Figure 2**), which is typical for very small platinum metal nanoparticles. [link below] The average size of the prepared nanoparticles is given in **Table 2**.

Table 2 Average size of the prepared nanoparticles (measured in nanometers)

Ruthenium	Rhodium	Osmium	Iridium	Platinum
5.1 ± 1.1	4.8 ± 1.3	1.3 ± 0.6	1.2 ± 0.3	4.4 ± 1.3

Except for iridium, whose dispersion was yellow, all the dispersions prepared were in shades of brown, and except for iridium and osmium, the dispersions were color stable. The iridium dispersion began to change color from yellow to light blue approximately one week after preparation. The reason for this color change is probably the recrystallization of nanoparticles. The dispersion of osmium was changed the intensity of color over time, this color change is observable about three weeks after preparation. The reason is probably the deposition of nanoparticles on the walls of the vessel.

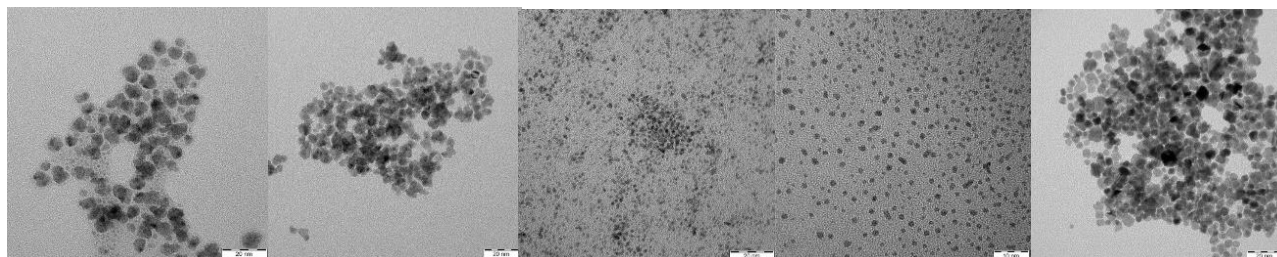


Figure 1 TEM images of nanoparticles a) Ru, b) Rh, c) Os, d) Ir, e) Pt (scale is 20 nm, only for Ir 10 nm)

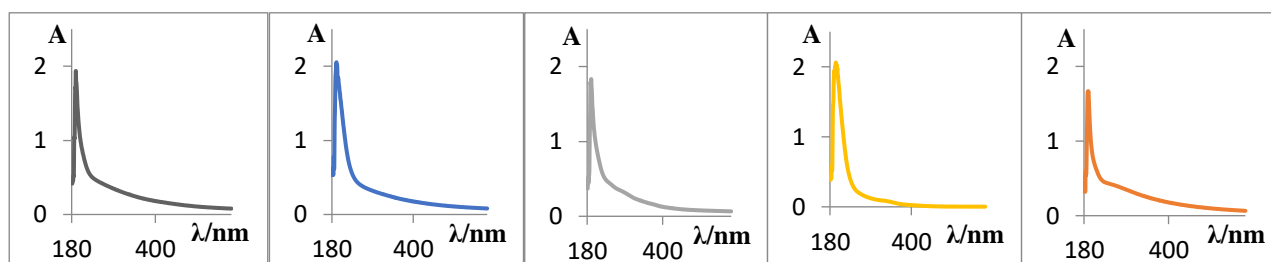


Figure 2 UV-vis spectra of aqueous dispersions of nanoparticles a) Ru, b) Rh, c) Os, d) Ir, e) Pt

3.2. Catalytic activity of nanoparticles

The catalytic activity of the prepared nanoparticles was studied using a model reaction, which was the reduction of 4-Nitrophenol (4-NP) to 4-Aminophenol. 4-Nitrophenol has a significant absorption peak at 401 nm, which decreases with reduction and a new peak appears around 300 nm, which belongs to 4-aminophenol. Since reductant NaBH₄ is in significant excess, it was possible to evaluate the used model reaction according to the kinetics of the pseudo-first order. For this reason, it was possible to subtract the rate constants as exponents in absolute value from the exponential regression equation from the graphs of the absorbance of 4-nitrophenol versus time. Absorbance values at 401 nm were used for this evaluation. When calculating the value of the rate constant, only the time interval in which the value of the logarithm of the absorbance decreased linearly was used from the graph of the dependence of the logarithm of absorbance on time. Thus, the time interval corresponding to the initiation period, in which the catalyst surface is activated in a strongly reducing environment and the primarily adsorbed particles are replaced by reactant molecules, was omitted from the calculation. To evaluate the effect of this slow part of the reaction, the reaction half-times $t_{1/2}$ were also subtracted from the measured kinetic curves, which better reflect the overall course of the catalytic reaction. The records of the spectra from the catalytic experiments are shown in **Figure 3**.

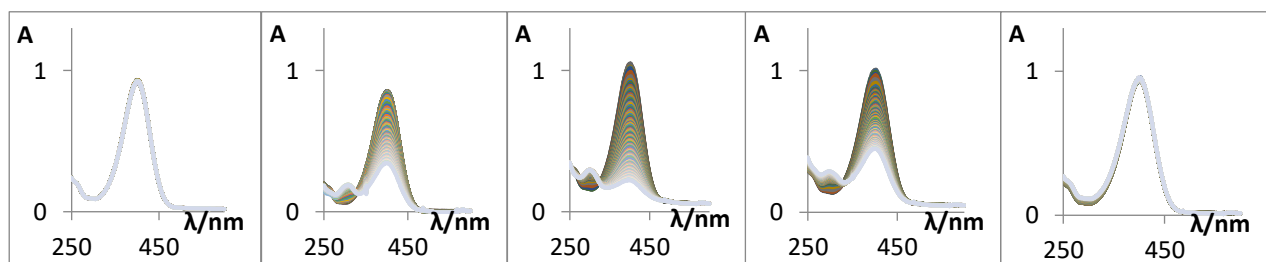


Figure 3 UV-vis spectra taken from the catalytic reaction of 4-NP reduction by borohydride a) without catalyst, b) catalysis of RuNPs, c) RhNPs, d) OsNPs, e) PtNPs, f) IrNPs

The average value of the rate constant for the reaction catalysed by ruthenium nanoparticles was the same as for the reaction catalysed by rhodium nanoparticles. However, the very long time was required to activate the Ru nanoparticle surface caused the reaction to be generally slower than in the case of Rh. This fact is also evidenced by the average value of the reaction half-time, which is almost 2.5 times higher for Ru than for Rh (**Table 3**).

As was already mentioned, the average value of the rate constant for the reaction catalysed by ruthenium nanoparticles is the same as in the case of Ru, but due to the much shorter time required for its activation, the reaction is faster. As a result, Rh nanoparticles (in this study) proved to be the best catalyst. A similar result was obtained in the study of Maegawa et al. [3].

The average value of the rate constant of the reaction catalysed by osmium nanoparticles makes it the third best catalyst. Iridium nanoparticles have proven to be the worst catalyst and the reaction catalysed by them practically does not run, even compared to the uncatalyzed reaction. These nanoparticles appear to be an

inhibitor of the observed reaction. However, the probable cause of a slight increase in absorbance (approximately 2%) is rather influenced by the aggregation of iridium nanoparticles in the reaction system. Platinum nanoparticles have proven to be the second worst catalyst in the reaction system used, but unlike other metals, this catalyst shows no initiation period.

Table 3 Rate constants and reaction half-times of 4-nitrophenol reduction with NaBH₄ in the presence of noble metal nanocatalysts

Metal	Rate constants (s ⁻¹)						k _{av} (s ⁻¹)	k _s (s ⁻¹)	t _{1/2av} (s)
Ruthenium	0.001	0.001	0.001	0.002	0.002	0.001	0.0013	0.0004	1250
Rhodium	0.001	0.001	0.002	0.002	0.001	0.001	0.0013	0.0004	485
Osmium	0.0005	0.0006	0.0006	0.0005	0.0006	0.0004	0.00053	0.0001	1275
Platinum	0.0002	0.0003	0.0002	0.0002	0.0003	0.0003	0.00025	0.00005	2990

k_s – rate constants normalised per 1 µg of catalyst

t_{1/2av} – reaction half-times obtained from the experimental kinetic curves (evaluated as average from six measurements)

4. CONCLUSION

The presented study was focused on methods of preparation of noble metal nanoparticles and study of their catalytic activity. The objective was to compare catalytic activity of these nanoparticles for redox reactions. Metal nanoparticles were prepared by the same method using sodium borohydride as primary reducing agent in the presence of sodium citrate as secondary reducing agent and stabilizer of the prepared nanoparticles. Successfully was prepared nanoparticles of ruthenium with an average diameter of 5.1 nm, nanoparticles of rhodium with an average diameter of 4.8 nm, nanoparticles of osmium with an average diameter of 1.3 nm, nanoparticles of iridium with an average diameter of 1.2 nm and nanoparticles of platinum of average size 4.4 nm. Palladium nanoparticles wasn't involved in this work because of problems with their preparation. The catalytic activity of the prepared nanoparticles was studied using model reaction based on reduction of 4-nitrophenol to 4-aminophenol with sodium borohydride at room temperature. Rate constants for reactions catalysed by nanoparticles of each metal were calculated using pseudo-first order kinetics. Rhodium nanoparticles have proven to be the best catalyst. Although the reaction catalysed by ruthenium nanoparticles had the same average rate constant as the reaction catalysed by rhodium nanoparticles, the very long time was required for activation of Ru catalyst. By this reason, ruthenium nanoparticles were worse catalyst than rhodium nanoparticles. Osmium nanoparticles were the third best catalyst. The second worst catalyst were platinum nanoparticles. The worst catalyst were iridium nanoparticles, which had no catalytic activity in the used reaction system.

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