Scientia Iranica F (2019) 26(3), 1925–1930

Sharif University of Technology
Scientia Iranica
Transactions F: Nanotechnology
http://scientiairanica.sharif.edu

Effect of HCl on the structure and catalytic activity of Pt/Al_2O_3 nanocatalyst prepared in microemulsion system

A. Keshavarz[a] **and A. Salabat**[a,b,*]

a. *Department of Chemistry, Faculty of Science, Arak University, Arak, 38156-8-8349, Iran.*
b. *Institute of Nanosciences & Nanotechnolgy, Arak University, Arak, 38156-8-8349, Iran.*

Received 29 September 2017; received in revised form 15 January 2018; accepted 14 May 2018

KEYWORDS
Nanocatalyst;
Pt nanoparticles;
Microemulsion;
Shape-controlled catalyst;
Catalyst activity.

Abstract. Nowadays, preparation of special and effective nanocatalysts is a hot research topic. Obviously, the size and structure of the active site of a catalyst plays a key role in catalytic activity. In this novel research, the Pt nanocatalyst supported on γ-Al_2O_3 was prepared in two different microemulsion systems to clarify the effect of microemulsion essence on catalyst character and activity. Two types of microemulsion systems were constructed from Triton X-100/2-butanol as surfactant and co-surfactant, i.e., *n*-heptane as organic phase and H_2O + H_2PtCl_6 (or HCl(aq) + H_2PtCl_6) as aqueous phase, to investigate the effect of HCl on the shape and structure of the prepared nanocatalysts. Shape, size, and size distribution of the Pt nanoparticles on the alumina were monitored by cyclic voltammetry and SEM analysis. Activity of the nanocatalysts was determined by reduction of *p*-nitrophenol as a reaction model.

1. Introduction

In recent years, the number of research studies in the field of catalysis has grown remarkably because of environmental and industrial needs, such as the need to remove air pollutants or the proposition of alternative energy sources. These studies aimed to investigate the influence of shape, size, size distribution, and composition of surface sites of the catalysts on their activity [1-3]. With the advent of nanotechnology and its application in catalytic reaction, the major step has been taken to design novel nanocatalysts [4-6]. The fabrication of metal nanoparticles with shape control and sizes is critical for catalytic applications. This subject has been confirmed by investigating platinum nanoparticle morphology, prepared in the presence of different capping polymers on their catalytic properties [7].

Long et al. prepared polyhedral and non-polyhedral Pt nanoparticles by a modified polyol method using $AgNO_3$ as a structure-modifying agent [8]. In addition, they reported on a polyol method used for fabricating stabilized Pt nanoparticles (Pt NPs) as cubic and octahedral shapes [9]. In another research work, published recently by Arán-Ais et al.[10], preferentially oriented (100) Pt NPs were synthesized by different methodologies and studied electrochemically.

Cuenya et al. published a review on the role of nanoparticle size and shape in chemisorption and catalytic performance [11]. They discussed the effect of the nanoparticles' shape and atomic structures on catalytic performance. Martinez-Rodriguez et al. synthesized Pt NPs by microemulsion method at different

---

*. *Corresponding author. Tel.: +98 86 32627530;*
Fax: +98 86 34173406
E-mail addresses: a-salabat@araku.ac.ir (A. Salabat); a-keshavarz@phd.araku.ac.ir (A. Keshavarz).

doi: 10.24200/sci.2018.5287.1184

HCl or H_2SO_4 concentrations [12,13]. They confirmed that cubic Pt nanoparticles could be obtained in the presence of HCl or H_2SO_4. In addition, they reported that the optimal HCl percentage in the water phase should be about 25% to obtain the highest amount of cubic nanostructures [14].

Further to our research works [15-17] and other literature results, we are encouraged to fabricate, for the first time, Pt/γ-Al_2O_3 nanocatalyst with controlling shape of Pt NPs dispersed on alumina using microemulsion systems. For this purpose, two different w/o microemulsion systems containing (H_2O + H_2PtCl_6)/*n*-heptane/Triton X-100/2-butanol and (HCl(aq) + H_2PtCl_6)/*n*-heptane/Triton X-100/2-butanol were used to prepare Pt/γ-Al_2O_3 nanocatalysts. The shape of the prepared Pt NPs in these two types of microemulsion systems was monitored electrochemically. Characterization of the synthesized nanocatalysts was also performed by XRD and SEM analysis. To determine catalytic activity of the nanocatalysts with different structures, reduction of *p*-NP over the prepared nanocatalysts was investigated.

2. Experimental procedures

2.1. Materials

Hexachloroplatinic acid (H_2PtCl_6) (99%), *n*-heptane, 2-butanol, and *p*-nitrophenol (*p*-NP) were obtained from Merck Company and used as received. The nonionic surfactant poly(ethylene glycol) *p*-(1,1,3,3-tetramethylbutyl)-phenyl ether (TX-100) with purity of 98% was purchased from Acros Company and used without further purification. Alumina (γ-Al_2O_3) was obtained from Japan Aerosil with the surface area of 110 m^2/g. All of the solutions were prepared by deionized water.

2.2. Preparation of Pt colloidal system

A colloidal system of platinum nanoparticles was prepared using a w/o microemulsion composed of *n*-heptane as oil phase, nonionic surfactant of TX-100, and co-surfactant of 2-butanol. Then, a suitable amount of 0.1 M aqueous solutions of H_2PtCl_6, prepared in pure water or aqueous 25% HCl, was added to a solution of *n*-heptane, TX-100, and 2-butanol to obtain microemulsion systems. Typical volume percentage of the microemulsion system includes 3% H_2PtCl_6 solution, 40.5% *n*-heptane, 16.5% TX-100, and 40% 2-butanol. The prepared microemulsion systems were stirred and settled down for 3 hours to equilibrate. Afterwards, the platinum precursor was reduced to the metallic Pt nanoparticles with the addition of NaBH4 to the microemulsion systems. In all experiments, the reducing agent ($NaBH_4$) to Pt molar ratio was kept at 10. The two different types of Pt colloidal systems (synthesized without and with HCl) are now ready for characterization or precipitation on the support and for producing nanocatalyst samples.

2.3. Fabrication of Pt/γ-Al_2O_3 nanocatalysts

In order to prepare the nanocatalysts' samples, the support of catalyst (γ-Al_2O_3) was added to the platinum colloidal systems. Then, Pt nanoparticles were harvested from colloidal suspensions with the dropwise addition of THF to precipitate platinum particles on the alumina support. Subsequently, the produced nanocatalysts of Pt/γ-Al_2O_3 were dried at room temperature for two days and, then, calcined at 600°C for 2 hours.

2.4. Characterization of nanocatalysts

A Philips diffractometer with Cu Kα radiation (Cu K α_1: 1.54056 Å, Cu K α_2: 1.54439 Å) was used to carry out X-ray diffraction (XRD) experiment on the produced nanocatalysts at room temperature. The 2θ angular region, with the step time of 0.02 s, between 20° and 80°, was considered.

To determine the size and size distribution of Pt NPs precipitated on alumina, the Scanning Electron Microscope (SEM) was applied using a MIRA3 TESCAN instrument.

The electrochemical characterization, as Cyclic Voltammetry (CV), of the platinum nanoparticles was carried out in an electrochemical cell with three electrodes. An AUTOLAB system of 101 (Eco Chemie Bv, the Netherlands) was used to control the electrode potential. A platinum wire was used as a counter electrode. To run the electrochemical experiments, the potentials were measured against a Reversible Hydrogen Electrode (RHE). A gold collector electrode was used to deposit the platinum nanoparticles over it and, finally, polished with alumina powder before each experiment. The electrolyte used for electrochemical characterization of the prepared electrode was 0.5 M of H_2SO_4 solution. The method for cleaning the Pt nanoparticles and CV condition was adjusted, as can be found in [13].

2.5. Catalytic activity test

In order to determine catalytic activity of the synthesized nanocatalysts with different structures, reduction of *p*-NP over the prepared nanocatalysts was investigated as a reaction model. The catalytic reduction of *p*-NP was performed in a stainless steel autoclave. The amount of 0.1 g catalyst and 10 ml aqueous solution of *p*-NP (with the initial concentration of 20 ppm) were added to the autoclave and sealed. In order to remove air, the autoclave was purged with hydrogen gas. Then, hydrogen gas was introduced into the reactor to a desired pressure. Finally, the hydrogenation reaction was performed at 303 K and 1 atm. The hydrogenation reaction progress was monitored by the intensity of the characteristic peak of

p-NP at 400 nm using the UV-vis spectrophotometer [18]. Catalytic conversion of p-NP reduction was calculated through the following equation:

$$\text{Conversion\%} = \frac{C_0 - C_t}{C_0} \times 100, \qquad (1)$$

where C_0 is the initial concentration of p-NP, and C_t is the concentration at various times of t.

3. Results and discussion

3.1. SEM analysis of the prepared nanocatalysts

The obtained SEM images of pristine γ-Al_2O_3 and Pt/γ-Al_2O_3 nanocatalysts, prepared in H_2O-microemulsion and HCl(aq)-microemulsion, are shown in Figure 1. It was found that the catalyst kept the layer structure of the γ-Al_2O_3 support and Pt nanoparticles well dispersed on the support. As can be seen from the size distribution histogram of Figure 1, the size of Pt nanoparticles is populated in the range of 2-10 nm for H_2O-microemulsion and 10-20 nm for HCl(aq)-microemulsion. Martínez-Rodríguez et al. observed the growth of the Pt particle size by increasing HCl concentration [13]. These results confirm that the growth step of the nanoparticles' synthesis in microemulsion systems depends considerably on the environmental conditions of the reaction.

3.2. X-ray diffraction spectroscopy of the prepared nanocatalyst

XRD patterns of the Pt/γ-Al_2O_3 nanocatalyst samples, prepared in H_2O-microemulsion and HCl(aq)-microemulsion, are shown in Figure 2. The main reflection angles shown in Figure 2, related to γ-Al_2O_3 or Pt,

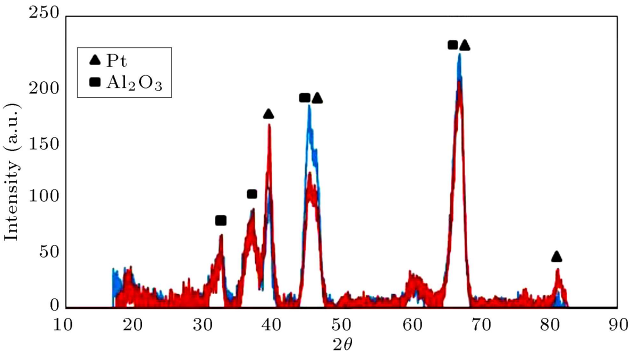
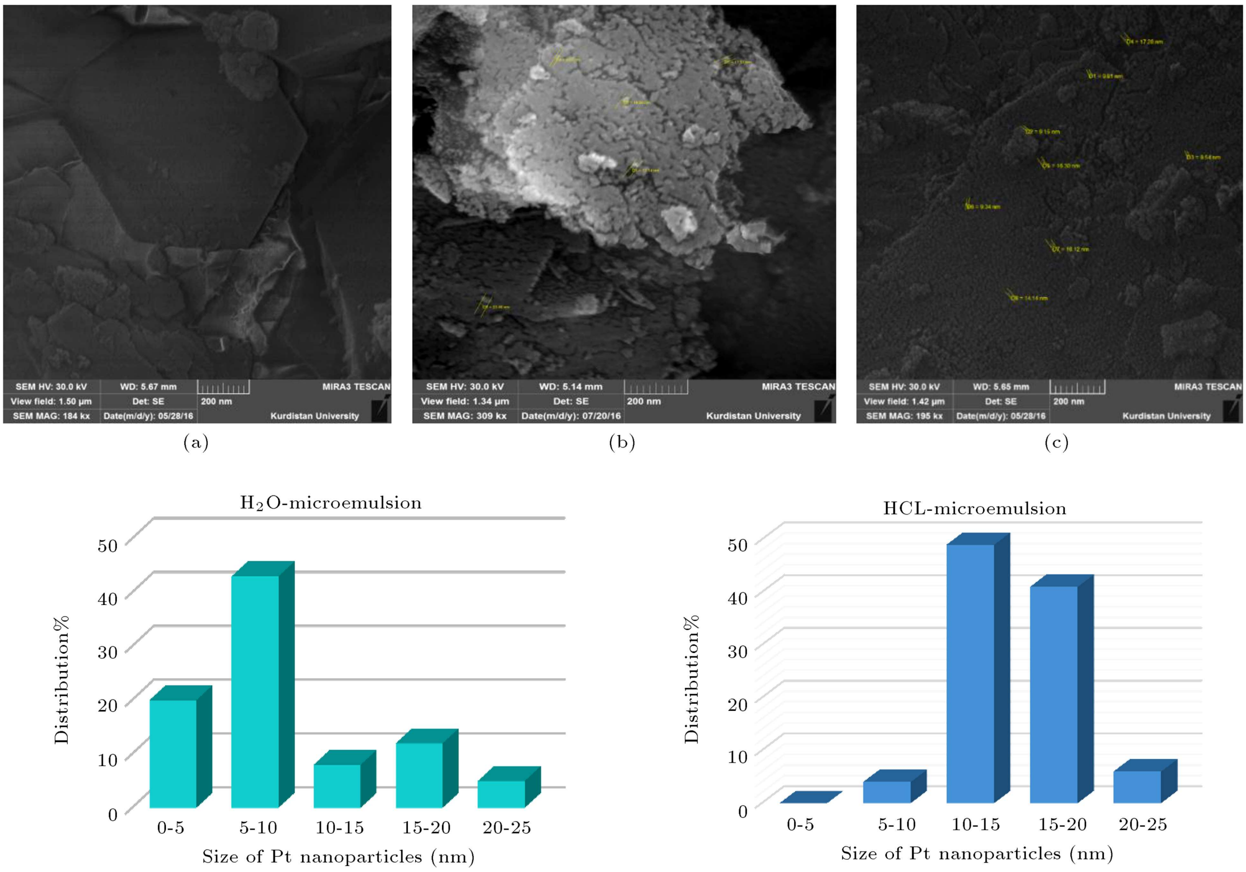


Figure 2. XRD patterns for Pt/γ-Al_2O_3 nanocatalysts (blue line) prepared in HCl-microemulsion and (red line) in H_2O-microemulsion systems.



(a) (b) (c)

Figure 1. SEM images of (a) γ-Al_2O_3, (b) Pt/γ-Al_2O_3 prepared in H_2O-microemulsion, and (c) Pt/γ-Al_2O_3 prepared in HCl-microemulsion and particle size distribution histogram of fabricated nanocatalysts.

have been approved by literature data. The reflection angles of $2\theta = 39.8°$, $46.4°$, and $66.8°$correspond to Pt(111), Pt(200), and Pt(220), respectively. As can be seen from XRD patterns, the two last peaks are overlapped at the same angles with alumina reflection data. As an interesting result, the intensity of surface (111) has been reduced and surface (200) increased for Pt nanoparticles synthesized in HCl(aq)-microemulsion system.

3.3. Electrochemical results

Cyclic voltammetry experiment on platinum nanoparticles, prepared in H_2O-microemulsion and HCl(aq)-microemulsion systems, was used to distinguish the effect of HCl on the shape of Pt particles. As reported by several investigations of CV for Pt NPs [13,14,19], four characteristic peaks of 0.12, 0.27, 0.37, and 0.53 V versus RHE should be observed. These peaks correspond to (110) sites, (100) steps and terrace borders, (100) terraces or wide domains, and (111) sites, respectively. Figure 3 shows CV for two types of nanoparticles, prepared in H_2O-microemulsion and HCl(aq)-microemulsion systems. As observed from CV results, the peak areas at 0.27 and 0.37 V considerably increased when Pt NPs were synthesized in HCl(aq)-microemulsion system, whereas the peak areas at 0.12 and 0.53 V decreased. The quantity of (111) sites is nearly negligible for the nanoparticles prepared in HCl (aq)-microemulsion system, which coincides with other observations [13,19].

3.4. Catalytic activity results

The hydrogenation reaction of *p*-NP, as a reaction model, over the Pt/γ-Al_2O_3 nanocatalysts was investigated to determine the effect of HCl in the fabrication process of catalyst on the catalyst activity. It is well known that Pt nanoparticles facilitate electron transfer from H_2 molecule, as a donor, to *p*-NP molecule as an acceptor [20]. As is shown in the following mechanism, a six-electron reduction process is necessary to transform *p*-NP to *p*-AP (*p*-aminophenol):

$$2\,Pt + H_2 \rightleftarrows 2\,Pt - H$$

$$6Pt - H + p - NP \rightarrow p - AP + 6Pt + 6H^+.$$

The reaction progress was monitored by measuring the absorption spectrum of *p*-NP as a function of time. After adding the Pt/γ-Al_2O_3 nanocatalysts to the reaction mixture of *p*-NP and H2, a gradual decrease in the absorption peak at 400 nm, related to *p*-NP, was observed. The preliminary experimental results confirmed that no hydrogenation reduction occurred in the absence of the catalysts. This result confirms that there is no non-catalytic reaction. The percentage of catalytic conversion of *p*-NP hydrogenation over Pt/γ-Al_2O_3 nanocatalysts synthesized in H_2O-microemulsion and HCl(aq)-microemulsion systems was calculated using Eq. (1), as reported in Table 1.

As a result, the efficiency percent of the catalytic reduction of *p*-NP over Pt/γ-Al_2O_3 nanocatalyst synthesized in HCl(aq)-microemulsion was found to be 100% after about 15 min. On the other hand, in the case of Pt/γ-Al_2O_3 nanocatalyst synthesized in H_2O-microemulsion system, the efficiency was observed as about 28.1% after 15 min (Table 1). This interesting result and excellent performance of the catalyst synthesized in HCl(aq)-microemulsion can be explained based on the structure of the Pt nanoparticles dispersed on the alumina. As explained by the electrochemical results, the obtained voltammetric profile of Pt/γ-Al_2O_3 nanocatalyst synthesized in HCl(aq)-microemulsion represents the largest contributions at 0.35-0.37 V relating to the (100) ordered domains (Figure 3). It means that the catalytic reduction of *p*-NP over Pt/γ-Al_2O_3 nanocatalyst is mainly accelerated by (100) site. On the other hand, this site can

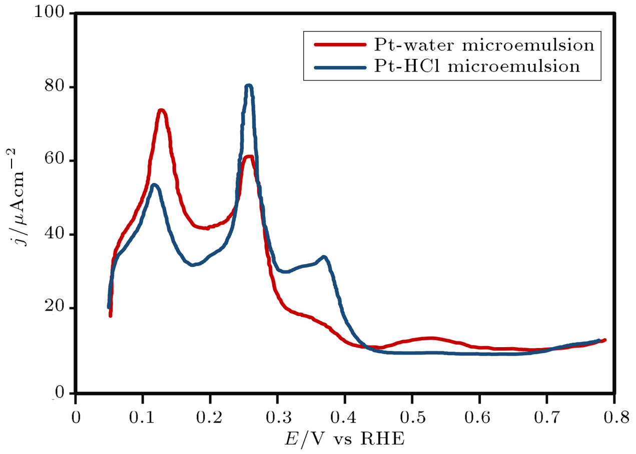


Figure 3. Voltameter diagram for platinum nanoparticles synthesized in water-microemulsion and HCl-microemulsion systems.

Table 1. Percentage of catalytic conversion of *p*-NP hydrogenation over Pt/γ-Al_2O_3 nanocatalysts synthesized in H_2O-microemulsion and HCl-microemulsion systems.

Time (min)	Pt/γ-Al_2O_3 Synthesized in water	Pt/γ-Al_2O_3 Synthesized in HCl 25%
5	4.8	26.2
10	11.9	95.1
15	28.1	100
20	45.8	100
25	51.8	100
30	58.3	100

facilitate electron transfer from donor H_2 to acceptor p-NP through the above mechanism.

4. Conclusion

In this research study, Pt/γ-Al_2O_3 nanocatalysts were prepared by using microemulsion method with different pH conditions for the first time. One w/o microemulsion contains (H_2O + H_2PtCl_6)/n-heptane/Triton X-100/2-butanol, and the other contains (HCl(aq) + H_2PtCl_6)/n-heptane/Triton X-100/2-butanol. Characterization of the prepared nanocatalysts by X-ray diffraction and cyclic voltammetric methods showed that HCl content had significant effect on the shape and activity of the nanocatalysts. The structure effect on the catalytic activity of the prepared nanocatalysts was investigated by hydrogenation reaction of p-NP, as a reaction model. It is concluded that the activity of Pt/γ-Al_2O_3 nanocatalyst synthesized in HCl(aq)-microemulsion with (100) preferentially oriented Pt nanoparticles is strongly more than that prepared in H_2O-microemulsion system. These results open a new avenue to regulate activity and selectivity of the nanocatalysts prepared in microemulsion systems.

Acknowledgment

The financial support from Arak University and Iran National Science Foundation is gratefully acknowledged (Grant No. 95818034).

References

1. Bennett, C.O. and Che, M. "Some geometric aspects of structure sensitivity", *J. Catal.*, **120**, pp. 293-302 (1989).
2. Bond, G.C. "Supported metal catalysts: some unsolved problem", *Chem. Soc. Rev.*, **20**, pp. 441-475 (1991).
3. Sánchez-Sánchez, C.M., Solla-Gullón, J., Vidal-Iglesias, F.J., Aldaz, A., Montiel, V., and Herrero, E. "Imaging structure sensitive catalysis on different shape-controlled platinum nanoparticles", *J. Am. Chem. Soc.*, **132**, pp. 5622-5624 (2010).
4. Oudar, J. "Hydrogenation reactions on platinum single crystals", *Zeitschrift für Physikalische Chemie*, **197**, pp. 125-136 (1996).
5. Englisch, M., Jentys, A., and Lercher, J.A. "Structure sensitivity of the hydrogenation of crotonaldehyde over Pt/SiO_2 and Pt/TiO_2", *J. Catal.*, **166**, pp. 25-35 (1997).
6. Kooti, M. and Afshari, M. "Magnetic cobalt ferrite nanoparticles as an efficient catalyst for oxidation of alkenes", *Scientia Iranica, F*, **19**, pp. 1991-1995 (2012).
7. Miyazaki, A., Balint, I., and Nakano, Y. "Morphology control of platinum nanoparticles and their catalytic properties", *J. Nanopart Res.*, **5**, pp. 69-80 (2003).
8. Long, N.V., Ohtaki, M., Hien, T.D., Jalem, R., and Nogami, M. "Synthesis and characterization of polyhedral and quasisphere non-polyhedral Pt nanoparticles: effects of their various surface morphologies and sizes on electrocatalytic activity for fuel cell applications", *J. Nanopart Res.*, **13**, pp. 5177-5191 (2011).
9. Long, N.V., Chien, N.D., Hayakawa, T., Matsubara, T., Ohtaki, M., and Nogami, M. "Sharp cubic and octahedral morphologies of poly(vinylpyrrolidone)-stabilised platinum nanoparticles by polyol method in ethylene glycol: their nucleation, growth and formation mechanisms", *J. Experimental Nanoscience*, **7**, pp. 133-149 (2012).
10. Arán-Ais, R.M., Solla-Gullón, J., Herrero, E., and Feliu, J.M. "On the quality and stability of preferentially oriented (100) Pt nanoparticles: An electrochemical insight", *J. Electroanal. Chem.*, **808**, pp. 433-438 (2018).
11. Cuenya, B.R. and Behafarid, F. "Nanocatalysis: size- and shape-dependent chemisorption and catalytic reactivity", *Surface Science Reports*, **70**, pp. 135-187 (2015).
12. Martínez-Rodríguez, R.A., Vidal-Iglesias, F.J., Solla-Gullón, J., Cabrera, C.R., and Feliu, J.M. "Synthesis and electrocatalytic properties of H_2SO_4-induced (100) Pt nanoparticles prepared in water-in-oil microemulsion", *Chem. Phys. Chem.*, **15**, pp. 1997-2001 (2014).
13. Martínez-Rodríguez, R.A., Vidal-Iglesias, F.J., Solla-Gullón, J., Cabrera, C.R., and Feliu, J.M. "Synthesis of Pt nanoparticles in water-in-oil microemulsion: Effect of HCl on their surface structure", *J. Am. Chem. Soc.*, **136**, pp. 1280-1283 (2014).
14. Martínez-Rodríguez, R.A., Vidal-Iglesias, F.J., Solla-Gullón, J., Cabrera, C.R., and Feliu, J.M. "Electrochemical characterisation of platinum nanoparticles prepared in a water-in-oil microemulsion in the presence of different modifiers and metal precursors", *Chem. Electro. Chem.*, **3**, pp. 1601-1608 (2016).
15. Soleimani, S., Salabat, A., and Tabor, R.F. "Effect of surfactant type on platinum nanoparticle size of composite Pt/α-Al_2O_3 catalysts synthesized by a microemulsion method", *J. Colloid Interface Sci.*, **426**, pp. 287-292 (2014).
16. Salabat, A. and Soleimani, S. "Ultrasonic irradiation and solvent effects on destabilization of colloidal suspensions of platinum nanoparticles", *Particuology*, **17**, pp. 145-148 (2014).
17. Soleimani, S. and Salabat, A. "Effect of various factors on the Pt nanoparticle size produced in a microemulsion system", *Colloid Journal*, **77**, pp. 207-212 (2015).
18. Pradhan, N., Pal, A., and Pal, T. "Silver nanoparticle catalyzed reduction of aromatic nitro compounds", *Colloid Surface A*, **196**, pp. 247-257 (2002).

19. Vidal-Iglesias, F.J., Arán-Ais, R.M., Solla-Gullón, J., Herrero, E., and Feliu, J.M. "Electrochemical characterization of shape-controlled Pt nanoparticles in different supporting electrolytes", *ACS Catalysis*, **2**, pp. 901-910 (2012).

20. Das, J., Aziz, M.A., and Yang, H. "A nanocatalyst-based assay for proteins: DNA-free ultrasensitive electrochemical detection using catalytic reduction of *p*-nitrophenol by gold-nanoparticle labels", *J. Am. Chem. Soc.*, **128**, pp. 16022-16023 (2006).

Biographies

Alireza Keshavarz is a PhD student of Physical Chemistry at Arak University, Iran. He received his MSc from Institute for Advanced Studies in Basic Sciences (IASBS) in 2013 in the field of physical chemistry. His research interests include surface chemistry and nanocatalyst.

Alireza Salabat is a Professor of Physical Chemistry at Arak University, Iran. He received BS (1991) in Applied Chemistry from Isfahan University of Technology and continued his field of study to obtain MSc (1994) and PhD (1998) from Tabriz University. He has worked as a Visiting Professor at Colloid Center of University of Bristol (2005-2006). His research interests include colloid science, surface chemistry, solution thermodynamics, polymer chemistry, nanocomposites, and nanocatalysts.