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**A study of different supports for the catalytic reduction of nitrates from natural water
with a continuous reactor.**

A.E. Palomares*, C. Franch, A. Corma

Instituto de Tecnología Química (UPV-CSIC). Universidad Politécnica de Valencia. Consejo Superior de Investigaciones Científicas. Avenida de los Naranjos s/n.46022 Valencia. Spain

Keywords: nitrate reduction, natural water, continuous reactor, support, Pd-Cu, Pd-Sn

Abstract

The aim of this work is to study the activity for the nitrate catalytic reduction in natural water, using a continuous stirred tank reactor, of Pd/Cu and Pd/Sn catalysts supported on different materials. The studied supports are: γ -Al₂O₃ (commercial), active carbon, graphite, hydrotalcite and alumina synthesized in our laboratory with a high surface area. The activity and selectivity of the catalysts supported on these materials have been compared. The best results have been obtained with the Pd/Sn catalysts supported on alumina. These results show that the surface area of the support is not the only important characteristic for an active catalyst in this reaction, being also very significant its acid-base properties, its electrical conductivity and its interaction with the metallic active sites. The adequate combination of these characteristics is necessary to obtain an active catalyst. The influence of the Pd/Sn content on the activity of the alumina supported catalysts was studied, observing that the best activity was obtained when the Pd/Sn ratio was higher than 1. This result clearly indicates that it is necessary to have both Pd and Pd-Sn centers in order to obtain an active catalyst.

1. Introduction

Nitrates groundwater pollution is an important problem in many populated areas from Europe and America. This pollution is mainly due to the use of fertilizers as well as to domestic and industrial effluents. In most of these areas, the natural water nitrate concentration is over the permissible limit for the human consumption that is 50 mg/L in Europe. There are different commercial techniques to remove nitrates from water as reverse osmosis and electrodialysis. They are effective but they generate a polluted waste that should be treated or disposed of [1]. Another possibility is the use of biological processes, based on the nitrates reduction to nitrogen using microorganisms [2] but there are concerns about possible bacterial contamination. A new technique that is actually under research is the catalytic reduction of nitrates to nitrogen, using hydrogen as reductant [2-9]. The catalysts used are based in a combination of a noble metal, such as Pd, Pt, Rh or Ir and a no noble metal, such as Cu, Sn, Ag or In [5-8, 10-14]. The problem of this reaction is the formation of undesired subproducts such as nitrites or ammonia. The activity of these catalysts was tested with different type of reactors [15-19] and by modifying the reaction conditions. It has been shown that better results are obtained by doing the reaction at an acid pH than without a pH control of the reaction [20, 21].

The activity of the catalyst is also influenced by the support used, in this way there are some articles that study the activity of different catalysts supported on different materials for the nitrate reduction reaction. These studies are mainly carried out in batch reactors and with distilled water containing only nitrates [4, 22-25]. Nevertheless, the presence of other ions in the reaction media could influence the activity and selectivity of the catalyst [26-28], for this reason it is important to study the activity of the bimetallic catalysts supported on different

materials, but using polluted natural water that contains other ions together with the nitrates and preferably with a continuous reactor.

The objective of this work is to study the nitrates catalytic reduction in natural water using Pd/(Sn or Cu) catalysts supported on different materials with a continuous stirred tank reactor.

2. Experimental

The supports used in this work in order to prepare the catalysts are: γ -Al₂O₃ (Merck), active carbon (Norit GAC 1240W), low density graphite (Sigma-Aldrich), Mg-Al hydrotalcite with a Mg/(Mg+Al) ratio of 0.25 (synthesized in our laboratory using the coprecipitation method) and a high surface area alumina (synthesized in our laboratory using the coprecipitation method). The surface areas of the supports are shown in Table 1. The bimetallic catalysts based in alumina, hydrotalcite or high surface area alumina were prepared by wetness impregnation using the soluble salts of the desired metals. The impregnation was made in two steps, first the support was impregnated with a SnCl₄·5H₂O or Cu(NO₃)₂·3H₂O solution, after that, the material was dried at 60°C for 4 hours and calcined at 500°C for 1 hour. In a second step, the catalyst was impregnated using a Pd(NO₃)₂·2H₂O solution, then the material was dried and calcined at 500°C for 1 hour. Finally, the catalyst was activated in a hydrogen flow at 500°C for 4 hours. On the other hand, the graphite and the active carbon were prepared by coimpregnation of the two metals (Cu or Sn and Pd) using the corresponding salt solution. The catalysts were dried at 100°C and reduced in hydrogen flow at 200°C for 1 hour.

The catalysts were tested in a continuous flow stirred tank reactor. Before starting the reaction, the water was bubbled with hydrogen during 1 hour. After that, the catalyst was introduced into the tank and a liquid flow rate of 5 mL/min was maintained during the reaction. The main characteristics of the water fed into the reactor are shown in Table 2. The

mass of the catalyst was 3 g and a mixture of CO₂ and H₂ (1:1) with a total flow of 500 cm³/min was introduced into the reactor during the reaction. The experiments were carried out at 20°C and atmospheric pressure. The stirring velocity of the reactor was 900 rpm. The reaction progress was followed by taking, at defined periods, small aliquots for the photometric determination of nitrate, nitrite and ammonia concentration. The measurements were done in an UV/VIS spectroscopy (Jasco UV/VIS spectrophotometer, model V-530) combined with reagent kits for the determination of nitrate (Spectroquant® nitrate test from Merck, measuring range 1–90 mg/L at 515 nm), nitrite (Spectroquant® nitrite test from Merck, measuring range 0.02–3 mg/L at 525 nm) and ammonia (Spectroquant® ammonia test from Merck, measuring range 0.01–3.5 mg/L at 690 nm).

3. Results and discussion

The catalysts were characterized by X-ray diffraction. In figure 1 it is shown the X-ray diffractogram of the catalyst containing 2.5%Sn and 5%Pd (% weight) supported on alumina. The diffractogram of the sample before activation shows the peaks associated to the support (γ -Al₂O₃) and the peaks assigned to PdO. After the activation, the PdO peaks disappear while new peaks associated to Pd metal appear, indicating that the PdO sites have been reduced to Pd and these sites have not been oxidized after reaction. Similar results were obtained with the other catalysts used in this work.

The activity for the nitrate reduction of the 2.5%Cu/5%Pd catalysts was studied on different supports: γ -Al₂O₃, Mg/Al hydrotalcite and graphite. The results obtained are shown in figure 2, as it can be seen the activity of the catalyst supported on alumina is higher than the activity of the catalysts supported on hydrotalcite or graphite, obtaining with the alumina supported catalyst a 95 % of nitrate conversion after 8 hours of reaction. There is not a deactivation of

the catalysts supported on alumina or hydrotalcite in this reaction time, only the catalyst supported on graphite shows a small deactivation after 4 hours of reaction.

On the other hand, the selectivity to ammonia (figure 3) is higher than 60% for the catalysts supported on alumina or hydrotalcite, whereas using graphite the selectivity is between 20-40%. These results represent a production of 17.8 ppm of ammonia with the catalyst supported on alumina, 8.3 ppm of ammonia for the catalyst supported on hydrotalcite and 3.8 ppm of ammonia for the catalyst supported on graphite. Nevertheless it has to be taken into account that the conversions obtained with the catalysts supported on hydrotalcite and graphite are much lower than that obtained with the catalyst supported on alumina, for this reason the formation of ammonia with the hydrotalcite and graphite supported catalysts cannot be directly compared with that of the alumina supported catalyst. The formation of nitrites was negligible with these catalysts.

The results obtained suggest that working in continuo with natural water and with a pH control, neither hydrotalcite, neither graphite are adequate supports for the Pd/Cu catalysts because the low activity shown by these materials. The low activity obtained with the catalyst supported on graphite can be related with its low surface area, but this cannot be the only reason for the different activities obtained with the catalysts supported on different materials. In fact, the catalysts supported on alumina or on hydrotalcite present a similar surface area but the results obtained with them are very different. This indicates that chemical properties of the support are also very important in order to have an active catalyst for this reaction. In this way, hydrotalcite is a basic material, while alumina presents some acidic properties, as it is shown by the pH of the point of zero charge (see table 3). According to [21], when the media pH is high, the catalyst surface is covered by hydroxide ions and the metallic active sites will be blocked by strongly adsorbed oxygen species leading to a drop in the activity. Although we

work with an acid pH and the media pH is controlled in our experiments by the continuous introduction of CO₂, a basic support as hydrotalcite generates a local basic environment in the support surface, producing the same problems. On the other hand, the combination of the high surface area and the acidic properties of the support could explain the best results obtained with the catalyst supported on alumina.

The activity of a Pd-catalyst containing tin instead of copper, supported on different materials was also studied. Contrary to what it occurred with the Pd/Cu catalysts, Pd/Sn catalysts present a high activity with all the studied supports (figure 4). The main difference observed within the Pd/Sn catalysts supported on different materials is the deactivation rate. As it can be seen, the best results are obtained with the catalysts supported on alumina and active carbon, both present a stable conversion around 80-90% during 8 hours of reaction, without any important deactivation. On the other hand, as it occurred with the Pd/Cu catalysts, the Pd-Sn catalysts supported on hydrotalcite and graphite show worse results than those obtained with the same catalyst supported on alumina or active carbon. The hydrotalcite supported catalyst shows initially a high activity (around 80%) but it deactivates quickly, reaching a 50% of conversion after 7 hours of reaction. The catalyst supported on graphite shows initially a very slow reaction rate, reaching the maximum activity after three hours of reaction and slowly deactivating after this maximum.

In figure 5 it is shown the selectivity towards ammonia of the Pd/Sn catalysts supported on the different materials. As it can be seen, the catalyst supported on active carbon shows an ammonia selectivity of 90%, whereas the same catalyst supported on alumina presents a selectivity of about 60%. These results represent a production of 14.7 ppm of ammonia with the catalyst supported on alumina and 26.6 ppm of ammonia for the catalyst supported on active carbon. The catalyst supported on hydrotalcite produces 9.3 ppm of ammonia and that

supported on graphite formed 11.1 ppm. The production of ammonia with these catalysts is lower than that produced with alumina, but it has to be taken into account that the conversion obtained with them is lower than that obtained with the other supports. The formation of nitrites was negligible with these catalysts.

Comparing the results obtained with the Pd/Sn catalysts supported on different materials with those obtained with the Pd/Cu catalysts, it is clear that the Pd/Sn catalysts present better activity than the Pd/Cu ones when using hydrotalcites or graphite as support. The difference is minor when the Pd/Sn is supported on alumina.

Regarding to the selectivity, the results show that Pd/Sn catalysts supported on alumina and hydrotalcite are more selective towards nitrogen than Pd/Cu catalysts. This is clear when using a hydrotalcite as a support. As it can be seen comparing figures 3 and 5, the Pd/Cu catalyst supported on a hydrotalcite, even presenting a lower nitrate conversion than the Pd/Sn catalyst is forming a higher quantity of ammonia. The worst selectivity towards nitrogen is obtained with the catalyst supported on active carbon. These results, obtained with nitrate polluted natural water are similar to those described in [29] obtained with distilled water containing nitrites. In that work is concluded that catalysts supported on carbon are more selective to ammonia as compared to oxidic supports. The reason for this has been explained by the electrical conductivity of the carbon supports [29] that increases the hydrogen surface coverage of Pd particles, resulting in an over reduction of the nitrate molecules that form ammonia instead of nitrogen. The electrical conductivity of the different supports has been measured using the system described in [30] and the results are shown in Table 2. As it can be seen the active carbon has the highest conductivity and it is the most selective towards ammonia as described in [29]. Nevertheless the graphite conductivity is only a bit lower than that of the active carbon but the selectivity towards nitrogen is much better than that obtained

with the active carbon catalyst. These results show that the catalyst electrical conductivity is not the only reason explaining the catalyst selectivity and other support characteristics are influencing the catalyst selectivity.

In order to check the catalyst deactivation, long-term reactions were made with the Pd/Sn catalysts supported on alumina, hydrotalcite and active carbon. All of them show some deactivation when using natural water. Nevertheless after 100 hours of reaction, a 58% conversion is obtained with the catalyst supported on alumina (see Figure 6), a 40% conversion is obtained with the catalyst supported on hydrotalcite and a 25% conversion is obtained with the catalyst supported on active carbon. The reason for this deactivation is probably related with the masking of the catalyst active sites [14]. This was checked by doing an experiment with the Pd/Sn catalyst supported on alumina but using distilled water containing nitrates instead of natural water. As it can be seen in Figure 6, when using distilled water although there is a partial catalyst deactivation after 100 hours of reaction, but it is less important than that observed when using natural water. This shows that the masking of the catalyst active sites is the most important reason for the catalyst deactivation, but it is not the only cause.

The results obtained indicate that the best catalyst is the Pd/Sn catalyst supported on alumina due to the high conversion obtained in the nitrate reduction reaction, to its stability and to the low selectivity to ammonia obtained at high conversion. Nevertheless, we have to point out that the selectivity to nitrogen obtained with this catalyst should be improved for a commercial use.

In order to clarify the role of the support surface area in the catalyst activity, we have prepared in our laboratory a high surface area alumina with 354.8 m²/g. We have compared the results obtained with a Pd/Sn catalyst supported on this material with those obtained with

a Pd/Sn catalyst supported on commercial alumina with a surface area of 138.5 m²/g (Table1). The results obtained are shown in figure 7. As it can be seen, there is only a small difference in the catalyst conversion obtained with both supports. The best results are obtained with the catalyst supported on a high surface area alumina in the first hours of the reaction, nevertheless after 8 hours of reaction the conversion obtained with both catalysts is very similar. There are no also important differences in the selectivity obtained with both catalysts, forming after 8 hours of reaction 14.7 ppm of ammonia with the catalyst supported on commercial alumina and 17.2 ppm of ammonia with the catalyst supported on high surface area alumina. The formation of nitrites was negligible with both catalysts. These results show that the catalyst surface area is initially important, because during the first hours of reaction, the highest conversion is obtained with the high surface area alumina supported catalyst. Nevertheless after some hours of reaction the differences in the catalyst activity are not so important, indicating that the catalyst surface area is not the only key factor determining the activity of the catalyst in this reaction.

We have studied the influence of the Pd/Sn ratio in the activity of the catalysts supported on alumina. Two type of experiments were made, one keeping constant the Pd content in 5% (weight) and modifying the quantity of tin (figure 8) and another one keeping constant the tin content in 1% (weight) and changing the Pd content (figure 9). As it can be seen in Figure 8, keeping constant the Pd content at 5% and modifying the Sn content, the best results are obtained when the Sn content is lower than the Pd content. Nevertheless it is necessary to have a certain tin content because the catalyst containing only palladium is practically inactive. These results prove that the presence of Pd metal centers together with Pd-Sn centers in the catalyst is required in order to obtain a good catalytic activity for this reaction. Similar results were obtained by keeping constant the Sn content at 1% and varying the Pd content.

As it can be seen in figure 9, the highest conversions are obtained with the catalysts containing a Pd/Sn ratio higher than one, because these catalysts have both Pd and Pd-Sn centers. On the other hand the catalyst that does not contain any Pd shows a negligible conversion. The results are coherent with the mechanism proposed in [21] suggesting that in the Pd-Sn centers the nitrates are reduced to nitrites, while nitrites are reduced to nitrogen or ammonia in the Pd centers. Regarding to the selectivity towards ammonia it has been described that ammonia is formed in Pd centers, for this reason a high Pd content results in a high selectivity to ammonia [31, 32]. From our results obtained using natural water instead of distilled water, this is not so clear, indicating that the presence of other ions in the media also influences the selectivity towards ammonia.

4. Conclusions

The study made about the catalytic reduction of nitrates in natural water using a continuous reactor concludes that the support used for the catalyst plays a key role in the reaction. The characteristics of the support that are more important in order to obtain an active catalyst are its acid-base characteristics, its electrical conductivity, the surface area and its interaction with the metallic active sites, being necessary an adequate combination of all of them in order to have an active support. In this way, when using natural water and working in continuo, the best catalytic support is a material that combines a surface area around 100-300 m²/g, acid characteristics and a low electrical conductivity, as alumina. The results obtained also show that Pd/Sn catalysts supported on alumina can be active catalysts for this reaction but it is necessary the presence of Pd and Pd-Sn centers, this is a Pd/Sn ratio higher than 1, in order to have an active catalyst. Nevertheless it should be pointed out that still the selectivity to nitrogen should be improved for a commercial use of this catalyst.

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Caption of tables and figures

Table 1. Surface area and conductivity of the supports studied.

Table 2. Main characteristics of the natural water used in the nitrates reduction reaction.

Table 3. pH of the point of zero charge (PZC) for different supports.

Figure 1. X-ray diffractograms of the catalyst 2.5%Sn-5%Pd/ γ -Al₂O₃ (% weight) before activation (a) and after reaction (b).

Figure 2. Catalytic hydrogenation of nitrates using natural water on 2.5%Cu/5%Pd (% weight) catalysts supported on Al₂O₃ (■), Mg-Al hydrotalcite (▲) and graphite (*).

Figure 3. Selectivity towards ammonia of the 2.5%Cu/5%Pd (% weight) catalysts supported on Al₂O₃ (■), Mg-Al hydrotalcite (▲) and graphite (*) in the catalytic hydrogenation of nitrates with natural water.

Figure 4. Catalytic hydrogenation of nitrates using natural water on 2.5%Sn/5%Pd (% weight) catalysts supported on Al₂O₃ (■), Mg-Al hydrotalcite (▲), active carbon (×) and graphite (*).

Figure 5. Selectivity towards ammonia of the 2.5%Sn/5%Pd (% weight) catalysts supported on Al₂O₃ (■), Mg-Al hydrotalcite (▲), active carbon (×) and graphite (*) in the catalytic hydrogenation of nitrates with natural water.

Figure 6. Catalytic hydrogenation of nitrates on 2.5%Sn/5%Pd (% weight) catalysts supported on Al₂O₃ using distilled water containing nitrates (○) and natural water containing nitrates (■).

Figure 7. Conversion (full line) and selectivity (dotted line) for the nitrates catalytic hydrogenation with natural water of the 2.5%Sn/5%Pd (% weight) catalysts supported on commercial γ -Al₂O₃ (■) and high surface γ -Al₂O₃ synthesized in our laboratory (◇).

Figure 8. Conversion (■) and selectivity (□) for the nitrates catalytic hydrogenation with natural water of the Al₂O₃ supported catalysts containing 5% Pd (weight) and different Sn contents after 4 hours of reaction.

Figure 9. Conversion (■) and selectivity (□) for the nitrate catalytic hydrogenation with natural water of the Al₂O₃ supported catalysts containing 1% (weight) Sn and different Pd contents after 4 hours of reaction.

Table 1

Supports	Conductivity (S/cm)	Surface area (m²/g)
Active Carbon Norit	18.09	1200
Graphite	12.66	0.2
Hydrotalcite	3.95*10 ⁻⁷	152.3
Alumina Merck	1.72*10 ⁻⁷	138.5
Alumina synthesized in laboratory		354.8

Table 1

Table 2

[NO ₃ ⁻] (mg/L)	[Fe ³⁺] (μg/L)	[Al ³⁺] (μg/L)	[Cl ⁻] (mg/L)	[SO ₄ ²⁻] (mg/L)	[Na ⁺] (mg/L)	[Ca ²⁺] (mg/L)	Conductivity (μS/cm)	pH
100	40	28	79	200	50	150	1000	8

Table 2

Catalyst	pH_{pzc}
2.5%Cu/5%Pd/Alumina	4.5
2.5%Cu/5%Pd/Hydrotalcite	11.5
2.5%Cu/5%Pd/Graphite	3.2

Table 3

Figure1

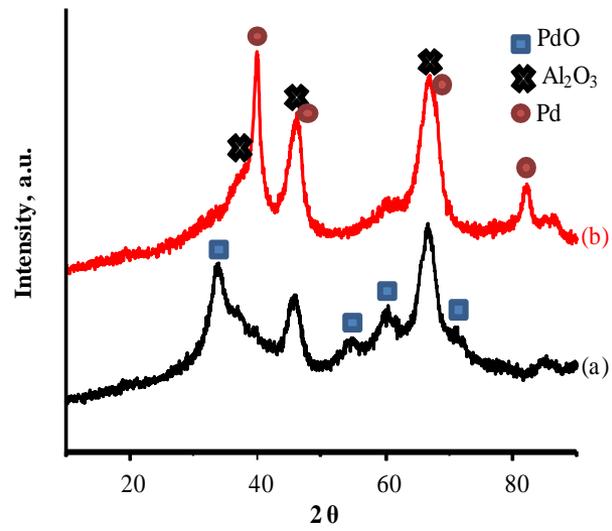


Figure 1

Figure2

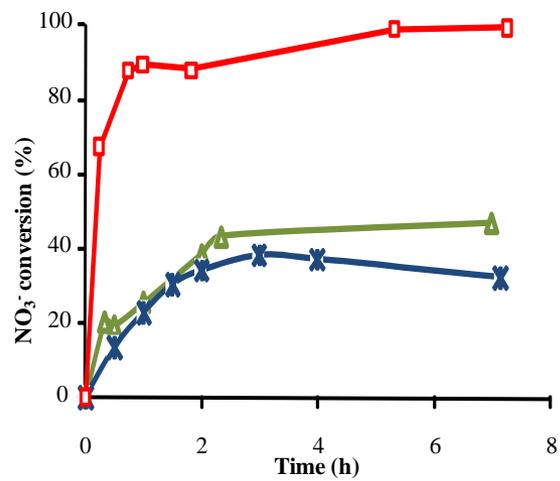


Figure 2

Figure3

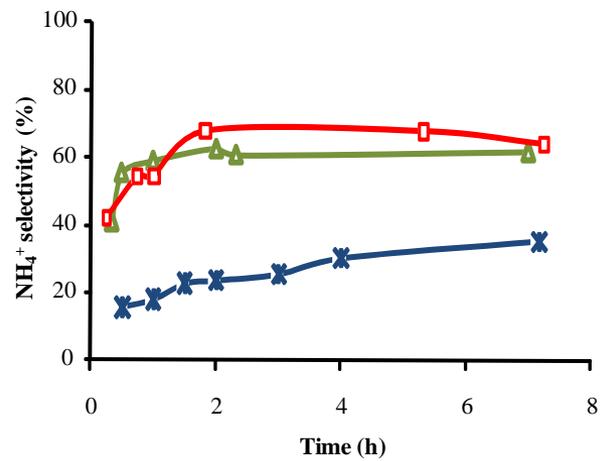


Figure 3

Figure4

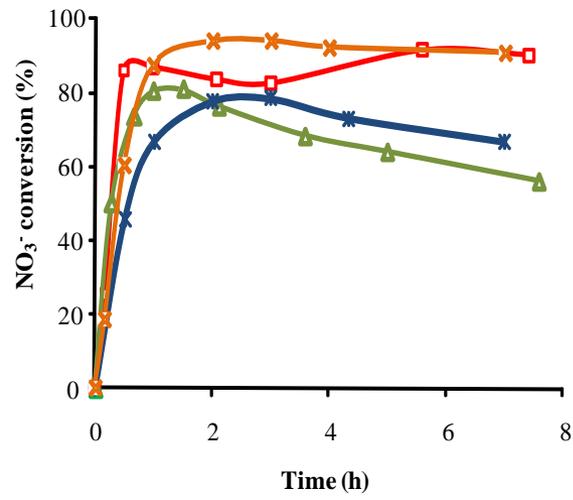


Figure 4

Figure5

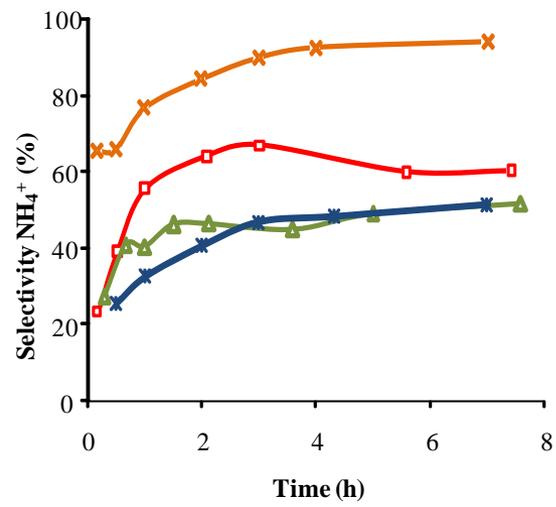


Figure 5

Figure 6

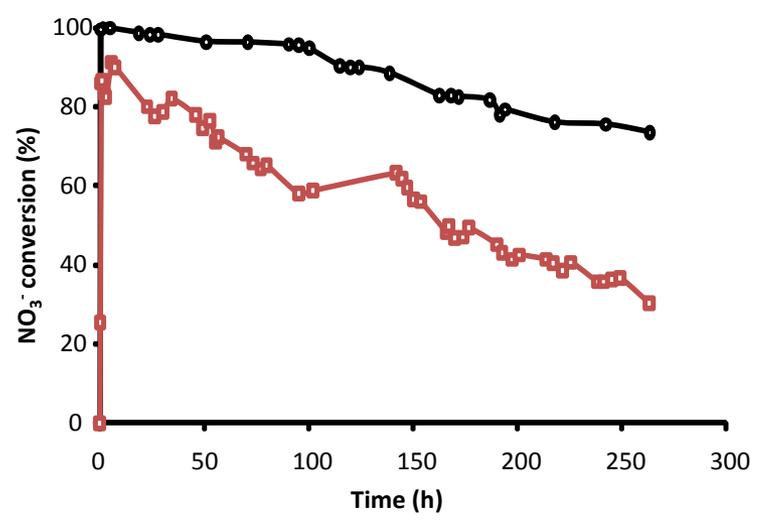


Figure 6

Figure 7

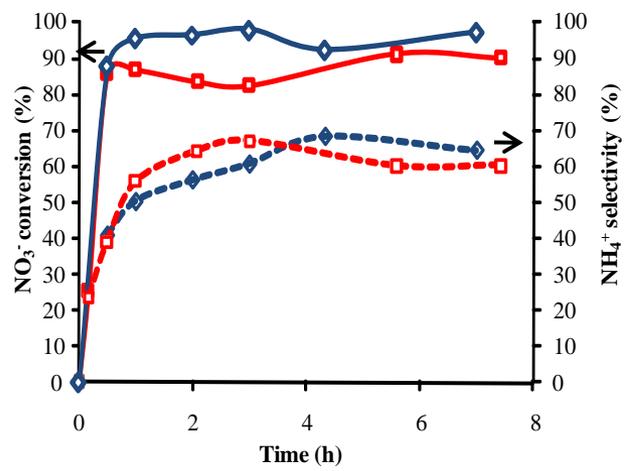


Figure 7

Figure 8

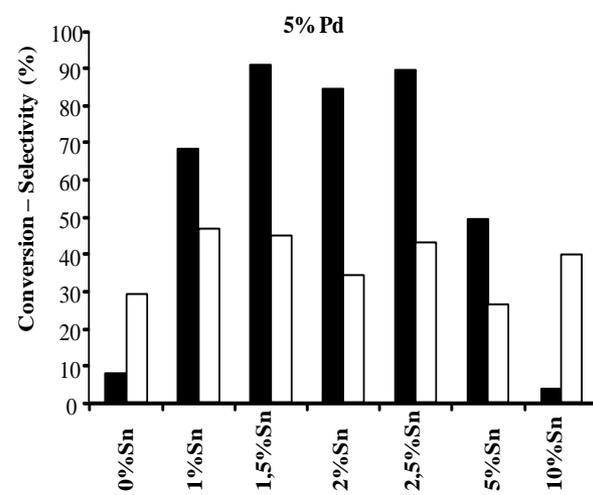


Figure 8

Figure 9

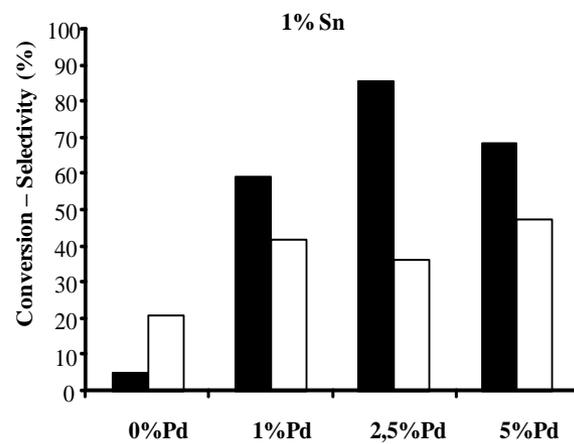


Figure 9