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Control of selectivity in the reduction of nitrate by shielding of Pd-Cu/C catalysts with AOT

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Abstract

Catalytic chemical reduction of nitrate without generating harmful nitrite and ammonium is still a challenge limiting the application of this technology to the production of drinking water. In this work a new approach was proposed based on shielding of Pd active sites in PdCu catalysts by sodium bis-2-ethylhexyl sulphosuccinate (AOT). To study this concept and the interactions between PdCu and AOT, carbon-supported PdCu catalysts were prepared by microemulsion using AOT as surfactant, and by incipient wetness impregnation followed by exposure to AOT. All the catalysts based on AOT showed lower activity in nitrate reduction than those prepared by ordinary incipient wetness impregnation, however ammonium generation was prevented thanks to shielding of Pd active sites by AOT. Bimetallic catalysts prepared by physically mixing Pd and Cu monometallic catalysts and exposure to AOT revealed a lower activity in nitrate reduction, which was ascribed to the interference of AOT in the Pd-Cu redox mechanism and lower hydrogen spillover. However, the catalysts maintained the ability to reduce nitrite with negligible production of ammonium, showing that shielding of Pd active sites can be an interesting approach to avoid nitrite and ammonium formation in nitrate reduction, but a compromise between activity and selectivity must be achieved.

Keywords: nitrate reduction, Pd-Cu catalysts, microemulsion, AOT, N₂ selectivity

List of abbreviations

AC	Activated carbon
AOT	Bis-2-ethylhexyl sulphosuccinate
IWI	Incipient wetness impregnation
ME	Microemulsion
NP	Nanoparticle
PMMC	Physical mixture of monometallic catalysts
w ₀	Water-to-surfactant ratio

1. Introduction

NO₃⁻ pollution of water bodies due to anthropogenic activities has generated a growing concern during the last decades [1, 2]. Studies on groundwater contamination by human activities suggest that NO₃⁻ pollution will increase in the next decades, acting as a driver for developing treatment technologies for the production of safe drinking water [3-5].

Different techniques have been proposed to remove NO₃⁻ from water [6-8], including physicochemical treatments and biological denitrification. Catalytic reduction has attracted growing attention due to its potential to reach a high NO₃⁻ conversion, relatively low operational costs compared with other techniques, and a harmless final product if selective reduction to N₂ is achieved. The catalytic reduction of NO₃⁻ with H₂ is a reaction with series and parallel routes: in a first step NO₃⁻ is reduced to NO₂⁻, then N₂ and/or NH₄⁺ are produced through intermediate species [9]. One of the major limitations of the catalytic reduction of NO₃⁻ is the formation of undesirable NO₂⁻ and NH₄⁺, whose maximum allowable concentrations in drinking water are 0.1 and 0.5 mg / L, respectively, according to the EU Directive 98/83/ECC.

Vorlop and Tacke [10] in their pioneering work reported the successful use of bimetallic catalysts for NO₃⁻ reduction. This reaction is usually performed with

1 bimetallic catalysts based on a noble metal (e.g., Pd, Pt, Rh) and a promoting transition
2 metal (e.g., Cu, Sn, In) [11,12]. PdCu system using a variety of supports is among the
3 most used due to its high ability to reduce NO_3^- [13,14].
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6 A redox process between noble metal and transition metal drives the reduction of NO_3^-
7 to NO_2^- on the transition metal active sites, in turn provoking oxidation of this metal.
8 Noble metals favor hydrogen spillover, which reduces the promoter thus closing the
9 redox cycle [9]. Besides, the noble metal allows reduction of NO_2^- to N_2 and/or NH_4^+ .
10 The metallic phase is usually supported on materials such as metal oxides [15,16],
11 zeolites [17] or carbon materials [14,18]. However, poor results have been usually
12 reported in literature in terms of selectivity to N_2 , which represent a major drawback
13 [19].
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16 In the last few years, photocatalytic [20], electrochemical [21] and combinations of
17 catalytic reduction and ion exchange [22] approaches have gathered much interest,
18 but removal of nitrate without producing nitrite or ammonium was not completely
19 achieved in most of the studies. Selectivity to N_2 of 100 % was reported by Kim et al.,
20 [23] using both catalytic reduction and ion exchange. This process is complex and
21 several stages are involved including regenerating exchange membrane at 6 bar, 60 °C
22 during 12 h under CO:H_2 flow and the subsequence production of brine that needs
23 additional treatment which difficult the large-scale application for drinking water.
24 Duan et al. [24] achieved 100% selectivity to N_2 using N-doped graphitic carbon-
25 encapsulated iron nanoparticles electrocatalysts and adding 1 g /L of NaCl, but without
26 NaCl the selectivity to N_2 decreased up to 25%. Therefore, after 30 years of research,
27 the effective catalytic reduction of nitrate is still an unsolved problem and, thus, new
28 approaches are needed.
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1 The main variables influencing reaction mechanism are operation conditions such as
2 pH, N:H molar ratio, but also catalyst structure and support [25-27]. The effect of the
3 catalyst structure on performance has drawn special attention since the development
4 of methods for the synthesis of metallic nanoparticles (NPs) with controlled size.
5 However, the capping agents and surfactants used in colloidal and microemulsion
6 synthesis of NPs cannot be removed easily from the catalyst surface after synthesis
7 [28], which can affect catalyst behavior [29-31].

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10 Interestingly, the interaction between metal NPs and capping agents and surfactants
11 can be a tool to modify catalytic behavior. In previous works [30,31] we studied the
12 chemical reduction of NO_2^- with catalysts based on size-controlled Pd NPs prepared by
13 microemulsion (ME), using sodium bis-2-ethylhexyl sulphosuccinate (AOT) as
14 surfactant. The surfactant had a significant effect on activity, and most noticeably on
15 selectivity, since shielding of Pd active sites by AOT resulted in complete inhibition of
16 the generation of NH_4^+ during the reduction of NO_2^- . However, to the best of our
17 knowledge, so far the effect of surfactants has not been explored in the direct catalytic
18 reduction of NO_3^- , even though ME techniques have been widely used for the synthesis
19 of mono and bimetallic catalysts.

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22 In the current work we have studied a new approach to develop catalysts without
23 ammonium production through the application of the concept of catalytic sites
24 shielding to bimetallic PdCu catalysts for NO_3^- reduction. The interaction between Pd,
25 Cu and AOT was systematically investigated through the preparation and testing of
26 different monometallic and bimetallic catalytic systems. The catalysts were prepared
27 via incipient wetness impregnation (IWI) and/or via ME. Likewise, selected catalysts

prepared by IWI were exposed to AOT before testing, with the aim of obtaining insight into the performance of catalyst where metal NPs were shielded by AOT.

2. Experimental

2.1 Materials

$\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ ($\geq 99.9\%$), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($\geq 99.9\%$), isooctane (99.8 %), methanol ($\geq 99.9\%$) and 2,2,2-Trifluoroethanol ($\geq 99\%$) from Sigma-Aldrich Co and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution (50-60 %) from Fluka were used as received. Sodium bis-2-ethylhexyl sulphosuccinate (AOT, 98 %, Sigma-Aldrich Co.) was vacuum-dried for 24 h at 333 K before use. Commercial Norit@SXPLUS activated carbon (AC) was supplied by Cabot Corporation. NaNO_3 ($\geq 99\%$) and NaNO_2 ($\geq 98\%$) were purchased from Panreac Química, SLU. H_2 ($> 99.999\%$) and CO_2 ($> 99.999\%$) were supplied by PRAXAIR. Demineralized bi-distilled water was used in this work.

2.2. Preparation of catalysts

The preparation of bimetallic PdCu catalysts and monometallic Pd and Cu catalysts was carried out by two ways: a) synthesis of metallic NPs via ME and deposition onto AC support, and b) IWI synthesis onto AC support. The catalysts were prepared with a nominal metal load of 1 % (wt., dry AC basis), and Pd:Cu mass ratio of 2 (1.2:1 mol ratio) in the case of the bimetallic catalysts.

The synthesis of NPs via ME was performed by reducing $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ and/or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with an aqueous solution of hydrazine (3M) in AOT/isooctane reverse micellar solution as described in our previous work [30]: the synthesis of Pd-AOT and Cu-AOT NPs was achieved by mixing two microemulsions of equal volume (67 mL): one

1 containing the metal precursor and other with the reducing agent. Each microemulsion
2 was prepared by mixing two solutions: one containing the metal precursor (0.05 M) or
3 the reducing agent (3 M) in water and other containing AOT in isooctane solution (0.35
4 M). These microemulsions were prepared using a water-to-surfactant molar ratio (w_0)
5 of 7. The microemulsions were mixed for 10 min of reduction time, then, isooctane
6 was evaporated in a rotary evaporator at 368 K and 150 mbar and the NPs were
7 purified from the excess of surfactant by the addition of methanol (40 mL) followed by
8 centrifugation (this washing procedure was repeated three times at 7000 rpm for 30
9 min). For the preparation of the carbon-supported catalysts, a suspension in methanol
10 of the NPs prepared by ME was mixed with AC in a rotary evaporator (Büchi) and
11 maintained at 368 K until complete removal of methanol. The mean size of the Pd
12 nanoparticles synthesized by microemulsion can be estimated in the 7-8 nm range, as
13 reported in previous works where the reproducibility of the synthesis was studied
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36 The IWI bimetallic PdCu catalysts were prepared by co-impregnation or successive
37 impregnation of the AC with aqueous solutions of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.
38 Bimetallic catalysts were also prepared by physical mixture of monometallic catalyst
39 (PMMC). The impregnating solution volume exceeded by 30 % the pore volume of the
40 AC support. Impregnation was followed by drying at room temperature for 2 h and
41 overnight at 333 K. Finally, the catalysts were calcined in air at 473 K for 2 h and
42 reduction was performed at 473 K for Pd catalysts and 573 K for Cu and PdCu
43 bimetallic catalysts under continuous H_2 flow of $60 \text{ N mL} \cdot \text{min}^{-1}$ for 2 h. In some
44 selected cases, IWI catalysts were also exposed to AOT to study the interaction
45 between Pd, Cu and AOT. Exposure of the catalysts was carried out by impregnation
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with a solution of AOT in ethanol at an AOT/metal molar ratio of 160 (which corresponds to the 50 % of the AOT used in ME synthesis), and then the catalysts were washed with methanol. The specific (BET) surface area, external (nonmicroporous) area and porous texture of the AC were obtained by means of N₂ adsorption–desorption isotherms at 77 K using a Micromeritics apparatus (Tristar II 3020 model). The specific surface area was 977 m²/g, the external area 329 m²/g and the micropore and mesopore volumes 0.31 and 0.34 cm³/g, respectively. Table 1 summarizes the catalysts synthesis and the corresponding nomenclature.

Table 1. Identification of the catalysts prepared

Catalysts	Type of catalyst	Method of synthesis	AOT exposure after synthesis
(PdCu) _{IWI}	Bimetallic	IWI, co-impregnation	No
(PdCu) _{IWI-AOT}	Bimetallic	IWI, co-impregnation	Yes
(PdCu) _{ME}	Bimetallic	ME, co-impregnation	-
Pd _{IWI} /Cu _{IWI}	Bimetallic	IWI, successive impregnation	No
Pd _{ME} /Cu _{IWI}	Bimetallic	ME (Pd), IWI (Cu), successive impregnation	-
Pd _{IWI} +Cu _{IWI}	PMMC	IWI	No
Pd _{IWI-AOT} +Cu _{IWI}	PMMC	IWI	Yes (Pd)
Pd _{IWI} +Cu _{ME}	PMMC	IWI (Pd) ; ME (Cu)	-
Pd _{ME} +Cu _{IWI}	PMMC	ME (Pd) ; IWI (Cu)	-
Pd _{ME} +Cu _{ME}	PMMC	ME	-

2.3 Nitrate and nitrite reduction tests

Catalytic reduction runs were carried out in batch upon 4 h in a three-necked jacketed glass reactor where CO₂ and H₂ were continuously fed both at 50 N mL min⁻¹ flow rate. Vigorous stirring was used to facilitate CO₂ and H₂ distribution through the solution. NO₃⁻ reduction experiments were performed with a reaction volume of 150 mL.

Initially, 1.5 g of catalyst and 140 mL of water were maintained under bubbling of CO₂ for 10 min to generate a buffered medium (pH ≈ 6). Then, 10 mL of NO₃⁻ stock solution were added to the reactor to achieve a NO₃⁻ starting concentration in the reaction medium of 100 mg / L. Afterwards, H₂ flow was connected and this event was considered as zero reaction time.

In the case of NO₃⁻ and NO₂⁻ simultaneous reduction tests, the starting concentration of 50 mg / L solution of NO₃⁻ was placed initially in the reactor, and after 60 minutes of reaction time a pulse of NO₂⁻ solution was injected into the reactor to reach a concentration of 50 mg / L for this ion. All the runs were carried out at atmospheric pressure and 303 K. The metal concentration in reaction medium was 100 mg / L. NO₃⁻ conversion and selectivity to NH₄⁺ and NO₂⁻ were defined according to Eqs. 1, 2 and 3, respectively:

$$X_{NO_3^-} (\%) = \frac{n_{NO_3^-,t=0} - n_{NO_3^-,t}}{n_{NO_3^-,t=0}} \cdot 100 \quad (1)$$

$$S_{NH_4^+} (\%) = \frac{n_{NH_4^+,t}}{n_{NO_3^-,t=0} - n_{NO_3^-,t}} \cdot 100 \quad (2)$$

$$S_{NO_2^-} (\%) = \frac{n_{NO_2^-,t}}{n_{NO_3^-,t=0} - n_{NO_3^-,t}} \cdot 100 \quad (3)$$

where $n_{NO_3^-,t=0}$ is the initial amount of NO₃⁻ (mmol) and $n_{NO_3^-,t}$, $n_{NO_2^-,t}$ and $n_{NH_4^+,t}$ are the amounts of the respective species at time t (min).

3. Results and Discussion

3.1 Nitrate reduction tests

Figure 1 shows the time course of NO₃⁻ concentration in the reduction runs carried out with IWI catalyst. The catalysts adsorbed approximately 70 – 80 % of the initial NO₃⁻,

1 which desorbed very fast when the H₂ flow was introduced in the reaction system,
2 thus causing steep rise of NO₃⁻ concentration at initial time. This suggests competition
3 between NO₃⁻ and H₂ for the catalyst surface. All the catalysts tested led to NO₃⁻
4 conversion higher than 95 % of in 1 h, and higher than 99 % in 4 h reaction time.
5 Interestingly, Pd_{IWI}+Cu_{IWI} catalysts showed NO₃⁻ conversion values as high as those
6 obtained with bimetallic catalysts. This is in good agreement with the works by Pintar
7 et al. [32] and Batista et al. [33], who reported that physical mixtures of monometallic
8 Pd and Cu catalysts supported on alumina gave NO₃⁻ conversion similar to that of
9 bimetallic catalysts, and proposed that PdCu active sites were generated *in-situ* by
10 collision between particles. Similar results were also obtained by Soares et al. [35],
11 who observed that physical mixtures of Pd and Cu catalysts supported on activated
12 carbon achieved NO₃⁻ conversions as high (95 %) as those obtained with bimetallic
13 ones after 300 min of reaction time, indicating that the conversion of NO₃⁻ could be
14 ascribed to *in-situ* formation of bimetallic catalysts as a result of adsorption of leached
15 copper. The results obtained in the current work indicate that the mixture of
16 monometallic catalysts had high activity from the beginning of the reaction test,
17 evidencing very fast *in-situ* generation of bimetallic sites, or contribution of an
18 additional mechanism. Yoshinaga et al. [18] also reported that physical mixtures of Pd
19 and Cu supported on activated carbon achieved a significant NO₃⁻ conversion (53 %)
20 although quite lower than that obtained with bimetallic catalysts (100 %). These
21 authors suggested that NO₃⁻ conversion with physical mixtures of monometallic Pd and
22 Cu catalysts could be ascribed not only to contact between catalyst particles but also
23 to hydrogen spillover from particles containing Pd to those containing Cu.
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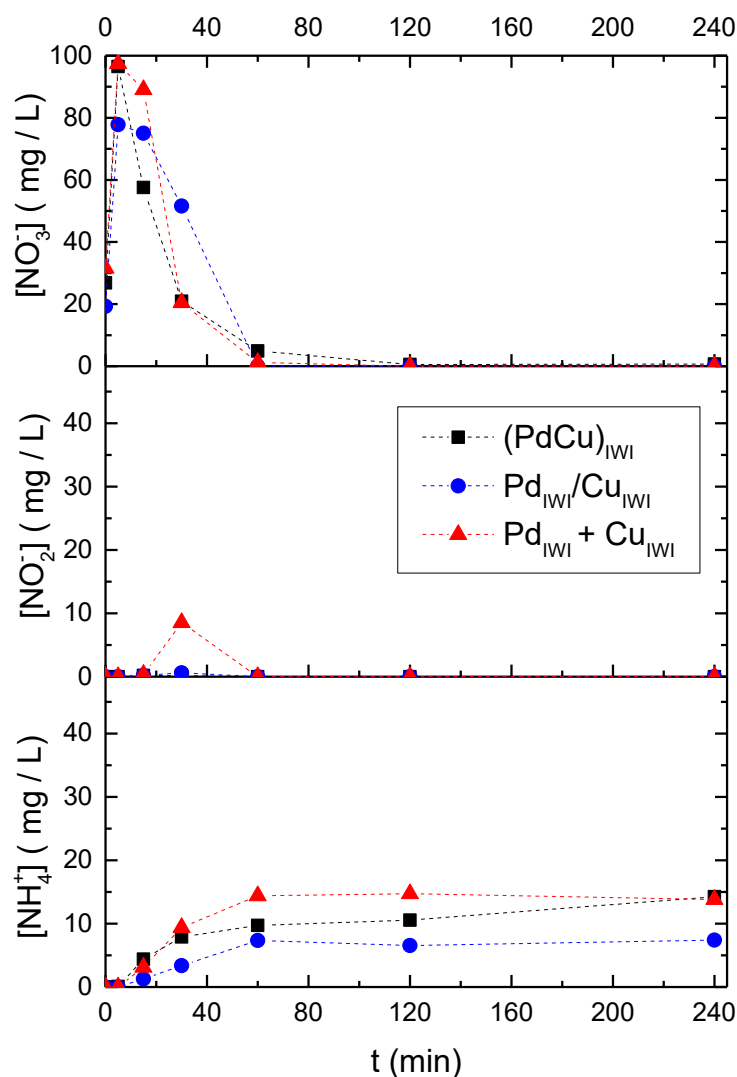


Figure 1. Time course of NO_3^- , NO_2^- and NH_4^+ upon reduction with IWI bimetallic catalysts prepared by co-impregnation, successive impregnation and as physical mixture of monometallic catalyst. $[\text{NO}_3^-]_0 = 100 \text{ mg/L}$.

Regarding selectivity, Figure 1 shows that a very low NO_2^- concentration was found in the case of bimetallic catalysts ($< 0.7 \text{ mg/L}$) along the NO_3^- reduction runs, whereas $\text{Pd}_{\text{IWI}} + \text{Cu}_{\text{IWI}}$ catalyst gave a peak concentration of about 9 mg/L . A significant amount of NH_4^+ was formed in all the runs in a range between approx. 7 and 14 mg/L .

1 The selectivity to NO_2^- and NH_4^+ versus NO_3^- conversion can be observed in Figure 2.

2 $\text{Pd}_{\text{IWI}}+\text{Cu}_{\text{IWI}}$ catalyst showed a higher selectivity to both species compared to bimetallic
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4 catalysts at equivalent NO_3^- conversion. In the case of NO_2^- , this observation can be
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6 ascribed to the distance between the Cu and Pd active centers in the physical mixture
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8 of monometallic catalysts. Thus, an accumulation of NO_2^- in the reaction medium is
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10 observed because the NO_2^- generated in Cu active sites has to migrate to Pd active
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12 sites in order to be reduced. Likewise, idle Pd centers can accumulate H_2 thus
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14 promoting the over-reduction of NO_2^- to NH_4^+ , as can be seen from the early
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16 occurrence of NH_4^+ in the reaction medium.
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22 The IWI PdCu bimetallic catalysts prepared by successive impregnation and co-
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24 impregnation also showed differences in the selectivity to NH_4^+ , which were explained
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26 by different distribution of active centers in the catalysts depending on the synthesis
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28 procedure [34]. A lower availability of Pd surface can be expected for the catalysts
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30 prepared by successive impregnation due to deposition of Cu on Pd, thus reducing also
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32 the spillover of H_2 and over-reduction to NH_4^+ .
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38 These experiments provide useful information on the different catalysts behaviour
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40 associated to the various synthesis procedures and the interaction between Pd and Cu,
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42 and help to understand the effect of active sites shielding by AOT on the catalysts
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44 performance, as discussed in the following sections.
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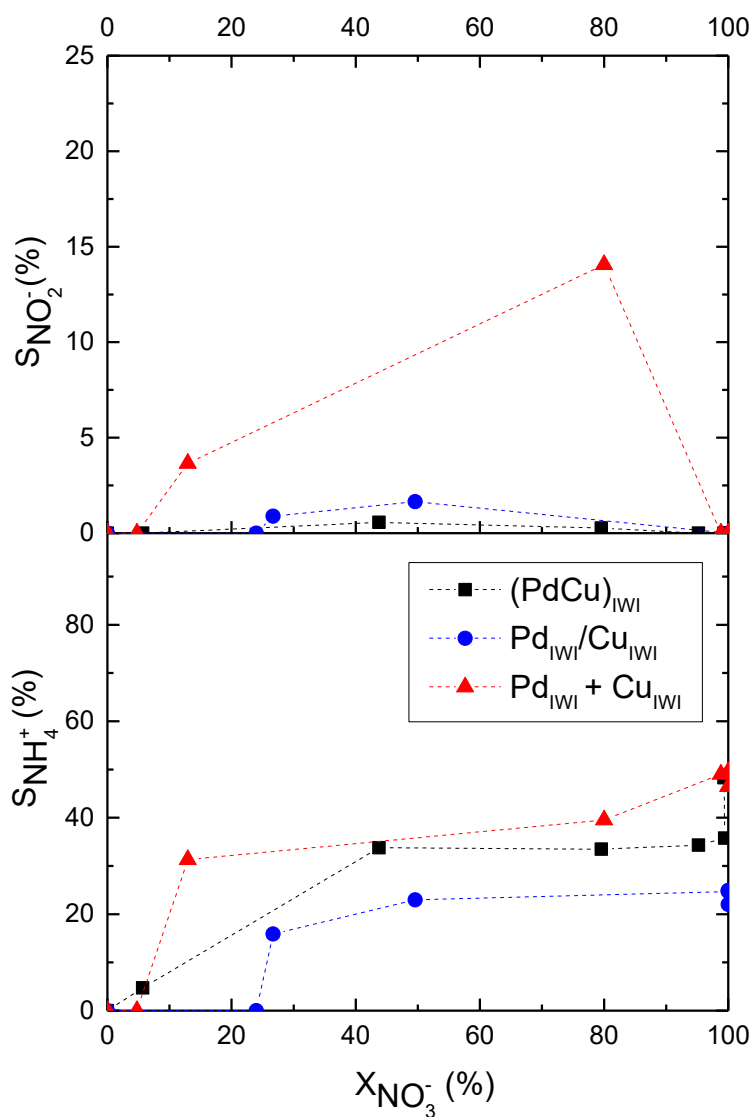


Figure 2. Selectivity to NO_2^- and NH_4^+ versus NO_3^- conversion upon reduction with IWI bimetallic catalysts prepared by co-impregnation, successive impregnation and as physical mixture of monometallic catalyst.

3.1.1 Effect of AOT on the performance of bimetallic catalysts

Figure 3 shows NO_3^- , NO_2^- and NH_4^+ concentration versus reaction time with selected bimetallic catalysts prepared by procedures involving ME synthesis. NO_3^- adsorption was significantly lower for those catalysts including NPs synthesized in presence of

1 AOT than for the ones prepared exclusively by IWI. This behaviour can be ascribed to
2 the strong interaction between AOT and metal NPs, particularly in the case of Pd, as
3 reported in a previous work [31]. However, Pd_{ME}/Cu_{IWI} catalyst exhibited important
4 initial adsorption of NO₃⁻, showing the relevant role of Cu in adsorption, probably due
5 to the preparation of Cu phase by IWI.
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10 PdCu bimetallic NPs catalyst prepared exclusively by ME, i.e. (PdCu)_{ME}, allowed a very
11 low NO₃⁻ conversion (~6 %), in contrast to the complete conversion achieved with
12 (PdCu)_{IWI}. Likewise, the catalyst prepared via IWI and afterwards exposed to AOT, i.e.
13 (PdCu)_{IWI AOT}, and the one prepared by successive impregnation via ME and IWI, i.e.
14 Pd_{ME}/Cu_{IWI}, yielded low to moderate NO₃⁻ conversion values of around 35 and 15 %, respectively.
15 All the catalysts compared in Figure 3 gave very low concentrations of
16 NO₂⁻ (< 0.7 mg / L), whereas significantly higher values were registered for NH₄⁺. The
17 Pd_{ME}/Cu_{IWI} catalyst led to the lowest concentration of NH₄⁺ (< 1 mg / L) and no
18 detectable NO₂⁻.
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36 The lower activity of the catalysts with NPs shielding by AOT can be ascribed to the
37 sulfonate group in its molecule, whose negative charge can compete with NO₃⁻ for
38 electron-deficient sites on metal NPs and also provoke NO₃⁻ repulsion. As indicated
39 above, this competitive adsorption is in good agreement with the very strong
40 interaction between AOT and Pd NPs reported in a previous work [31]. Likewise, the
41 specific surface area of the catalysts can decrease after impregnation of the NPs
42 synthesized by ME, due to AOT incorporation into the support, even after purification
43 of the NPs [30]. Interestingly, the active sites on the surface of Cu NPs are main
44 contributors to the reduction of NO₃⁻ into NO₂⁻, but in catalysts (PdCu)_{ME} and (PdCu)_{IWI}
45 AOT these sites seemed also to be shielded or not active. The lack of activity of these
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catalysts could be related to diminished hydrogen spillover from Pd to Cu due to shielding.

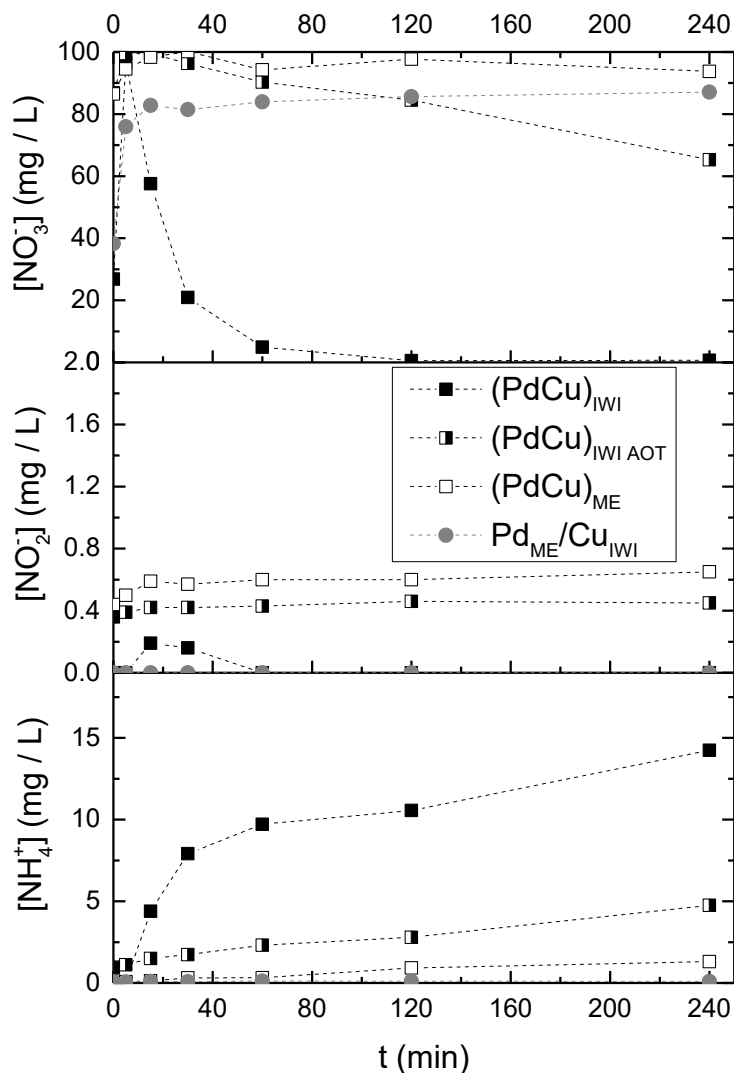


Figure 3. Time course of NO_3^- , NO_2^- and NH_4^+ upon reduction with bimetallic catalysts prepared with procedure involving AOT. $[\text{NO}_3^-]_0 = 100 \text{ mg / L}$.

Figure 4 shows the selectivity to NO_2^- and NH_4^+ versus NO_3^- conversion with selected bimetallic catalysts prepared by procedures involving ME synthesis. At NO_3^- conversion values below 5 %, $(\text{PdCu})_{\text{IWI}}$ catalyst did not show selectivity to NO_2^- , which contrasts

1 with the observed with (PdCu)_{IWI AOT} and (PdCu)_{ME} catalysts (between 1 and 5 %). These
2 catalysts were capable of reducing NO₂⁻, whose concentration decreases to negligible
3 values at long reaction times. In the case of non-supported and carbon-supported
4 monometallic Pd NPs synthesized by ME it has been reported that they maintain the
5 ability for NO₂⁻ reduction, but activity is diminished [30,31]. The procedure for the
6 preparation of the catalyst with shielded NPs, i.e the way the metal is exposed to AOT,
7 also affects to selectivity, as indicated by the fact that Pd_{ME}/Cu_{IWI} catalyst did not show
8 selectivity to NO₂⁻.
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10 Regarding to the selectivity to NH₄⁺, no significant differences were found at low NO₃⁻
11 conversion (≤ 15 %). Beyond a NO₃⁻ conversion of around 20 % the Pd_{ME}/Cu_{IWI} catalyst
12 showed a selectivity to NH₄⁺ below 1 %, whereas that of (PdCu)_{IWI AOT} was close to 4 %.
13 It is worthy to note that selectivity to NH₄⁺ of (PdCu)_{IWI} was significant, and much
14 higher than that of (PdCu)_{IWI AOT} at NO₃⁻ conversion values of around 40 %. Therefore,
15 shielding of catalysts with AOT is a feasible approach to reduce the production of NH₄⁺
16 during the catalytic chemical reduction of NO₃⁻.
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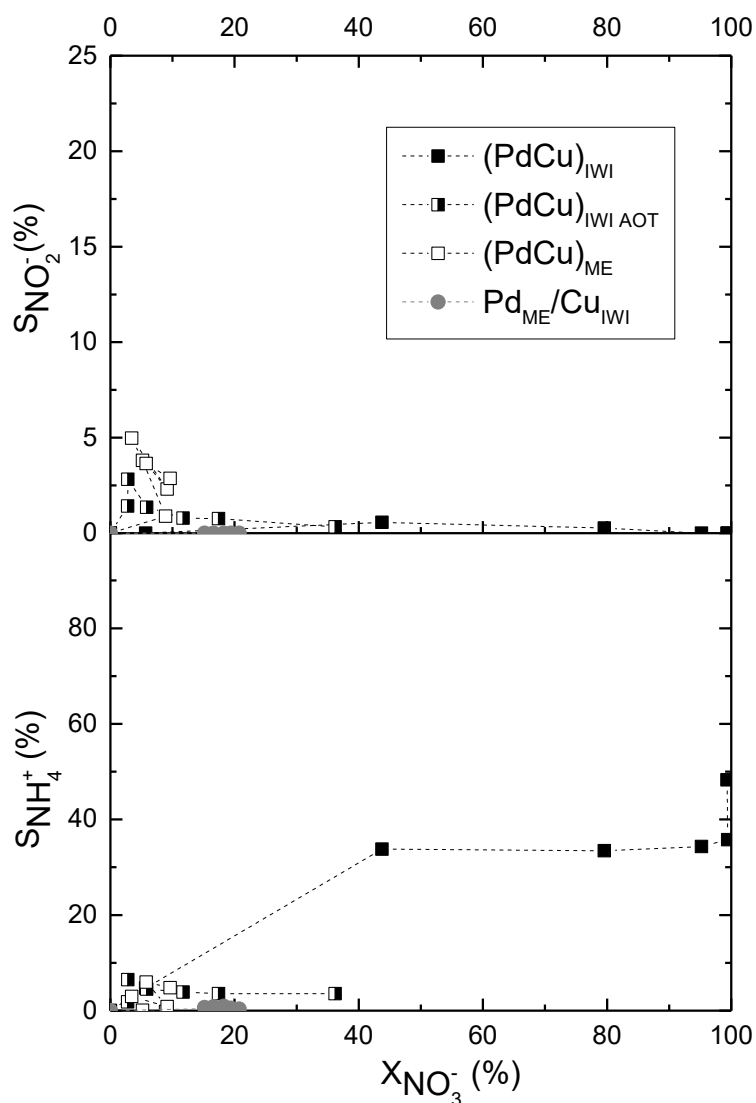


Figure 4. Selectivity to NO_2^- and NH_4^+ versus NO_3^- conversion with bimetallic catalysts

3.1.2 Effect of AOT in the performance of catalysts prepared by physical mixture of monometallic catalysts

Runs using PMMC prepared via IWI and ME were performed in order to gain insight on the shielding of active sites by AOT. Figure 5 shows NO_3^- , NO_2^- and NH_4^+ concentrations versus reaction time with these catalysts. $Pd_{IWI}+Cu_{IWI}$ and $Pd_{IWI}+Cu_{ME}$ yielded significantly higher NO_3^- conversion than $Pd_{ME}+Cu_{IWI}$ and $Pd_{ME}+Cu_{ME}$.

Moreover, differences in activity between $\text{Pd}_{\text{IWI}}+\text{Cu}_{\text{IWI}}$ and $\text{Pd}_{\text{IWI}}+\text{Cu}_{\text{ME}}$ were observed, indicating that shielding of Cu sites also led to a decrease in activity. Probably AOT interferes in the redox reaction between Pd and Cu and thus, in the formation of bimetallic sites [35].

NO_2^- concentration in the reaction medium was in the 0-0.8 mg / L range for all the catalysts, with the exception of $\text{Pd}_{\text{IWI}}+\text{Cu}_{\text{IWI}}$ which peaked around 9 mg / L. Since $\text{Pd}_{\text{IWI}}+\text{Cu}_{\text{IWI}}$ and $\text{Pd}_{\text{IWI}}+\text{Cu}_{\text{ME}}$ catalysts were the only two yielding high NO_3^- conversion (> 95 %), this suggests that shielding of Cu sites also prevented the production of NO_2^- . NH_4^+ concentration at long reaction times was between 14 - 18 mg / L for the most active catalysts, and between 0 - 0.8 mg / L for the rest.

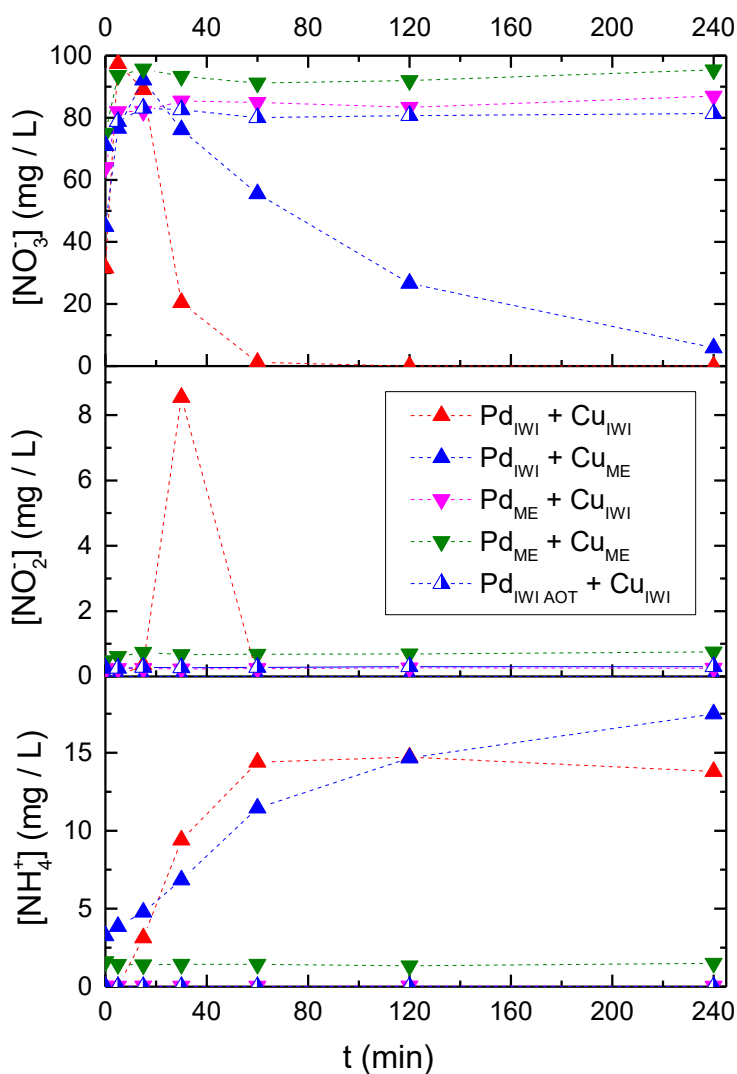


Figure 5. Time course of NO_3^- , NO_2^- and NH_4^+ upon reduction with PMMC prepared using ME and/or IWI. $[\text{NO}_3^-]_0 = 100 \text{ mg/L}$.

Figure 6 depicts the selectivity to NO_2^- and NH_4^+ versus NO_3^- conversion with PMMC catalysts. $\text{Pd}_{\text{IWI}} + \text{Cu}_{\text{IWI}}$ and $\text{Pd}_{\text{IWI}} + \text{Cu}_{\text{ME}}$ showed significant differences in selectivity to NO_2^- , being lower for the second, which can be ascribed to interaction of AOT with Cu, decreasing the reduction rate of NO_3^- to NO_2^- , thus attenuating NO_2^- peak. This can also

1 be observed with Pd_{IWI}+Cu_{ME} and Pd_{ME}+Cu_{ME}, since their selectivity to NO₂⁻ was
2 equivalent at ca. 10 % NO₃⁻ conversion.
3

4 Relevant results can be observed regarding the selectivity to NH₄⁺. Pd_{IWI}+Cu_{ME} catalyst
5 showed a significantly higher selectivity to that species than Pd_{IWI}+Cu_{IWI}. This can be
6 ascribed to lower production of NO₂⁻ in the case of the former, which allows a higher
7 H/N ratio on the Pd surface, favoring over-reduction of NO₂⁻ to NH₄⁺. On the other
8 hand, catalysts with shielded Pd active sites, i.e. Pd_{ME} or Pd_{IWI} AOT, showed extremely
9 low selectivity to NH₄⁺, indicating that it can be controlled by Pd-AOT interaction, via
10 ME synthesis or exposure to AOT after IWI synthesis, although at the expense of
11 activity.
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25 Evidences of the shielded Pd active sites can be found in former works dealing with
26 monometallic Pd NPs. Selective washing of Pd-AOT nanoparticles with acidic and polar
27 solvents (trifluoroethanol) enabled removal of AOT strongly interacting with low-
28 coordination and electron-deficient species on the surface of the Pd NPs, thus
29 increasing the activity of the nanoparticles in the reduction of nitrite ion and the
30 generation of ammonium [R1]. An increase of activity of Pd-AOT nanoparticles was
31 also achieved when removal of AOT was performed by thermal treatment in inert
32 atmosphere [R2]. However, XPS characterization of Pd-AOT nanoparticles subjected to
33 thermal treatment in inert atmosphere indicated that some fragments of AOT are still
34 remaining on the surface of Pd nanoparticles, mostly CH₃(CH₂)S- species and Pd-S
35 bonds indicating the strong interaction between S and Pd. [R3]. On the contrary, after
36 thermal treatment with air, the intensity of this peak decreased as well as the peak
37 associated to R-SO₃⁻ head group of AOT and the nanoparticles exhibited even higher
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activity. This strong interaction between AOT and Pd nanoparticles is expected also to occur to in PdCu catalysts and is consistent with the results observed.

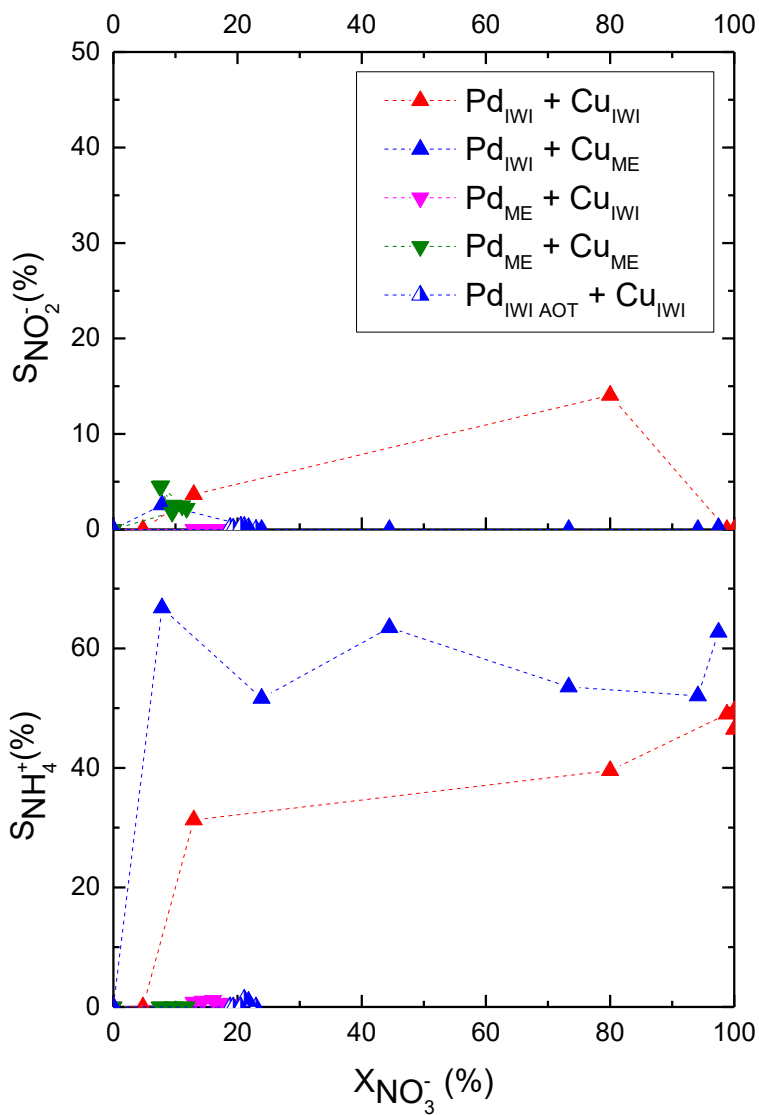


Figure 6. Selectivity to NO_2^- and NH_4^+ versus NO_3^- conversion for the PMMC catalysts

3.2 Simultaneous nitrate and nitrite reduction tests

Simultaneous NO_3^- and NO_2^- reduction tests were performed to further analyze the effect of AOT shielding in the first and second steps of the reaction pathway. Catalysts showing low activity in previous NO_3^- reduction runs were also considered. Figure 7

shows NO_3^- , NO_2^- and NH_4^+ evolution upon reaction time for $\text{Pd}_{\text{ME}}+\text{Cu}_{\text{IWI}}$ and $(\text{PdCu})_{\text{IWI}}$ AOT catalysts. As it was described in the experimental section, these tests were carried out with a starting NO_3^- concentration of 50 mg / L. Both catalysts showed very low activity in NO_3^- reduction, with fairly low conversion even after 7 h of reaction. However, when NO_2^- was injected into the reaction system (time= 60 min) it was rapidly reduced, indicating that AOT did not shield completely the Pd active centers responsible of NO_2^- reduction. This result suggests again that the interference of AOT in Pd and Cu redox reaction is a main cause of the low activity in NO_3^- reduction. The lower selectivity to NH_4^+ observed for $\text{Pd}_{\text{ME}}+\text{Cu}_{\text{IWI}}$ shows that the synthesis of Pd NPs by ME allows more effective shielding of Pd active sites by AOT, blocking the active sites associated with the production of NH_4^+ , and/or attenuating build-up of nitrogen species precursors of NH_4^+ . The high NH_4^+ generation with $(\text{PdCu})_{\text{IWI}}$ AOT indicates that mere exposure of IWI bimetallic catalysts to AOT cannot avoid completely the generation of this species. A clearer comparison can be seen in Figure 8, where NH_4^+ selectivity versus NO_2^- conversion is shown. $(\text{PdCu})_{\text{IWI}}$ AOT catalyst yielded negligible selectivity to NH_4^+ for NO_2^- conversion values lower than ca. 50%. At higher conversion the selectivity increased, indicating that the bimetallic catalyst prepared by co-impregnation and subsequent exposure to AOT cannot control the selectivity to NH_4^+ effectively.

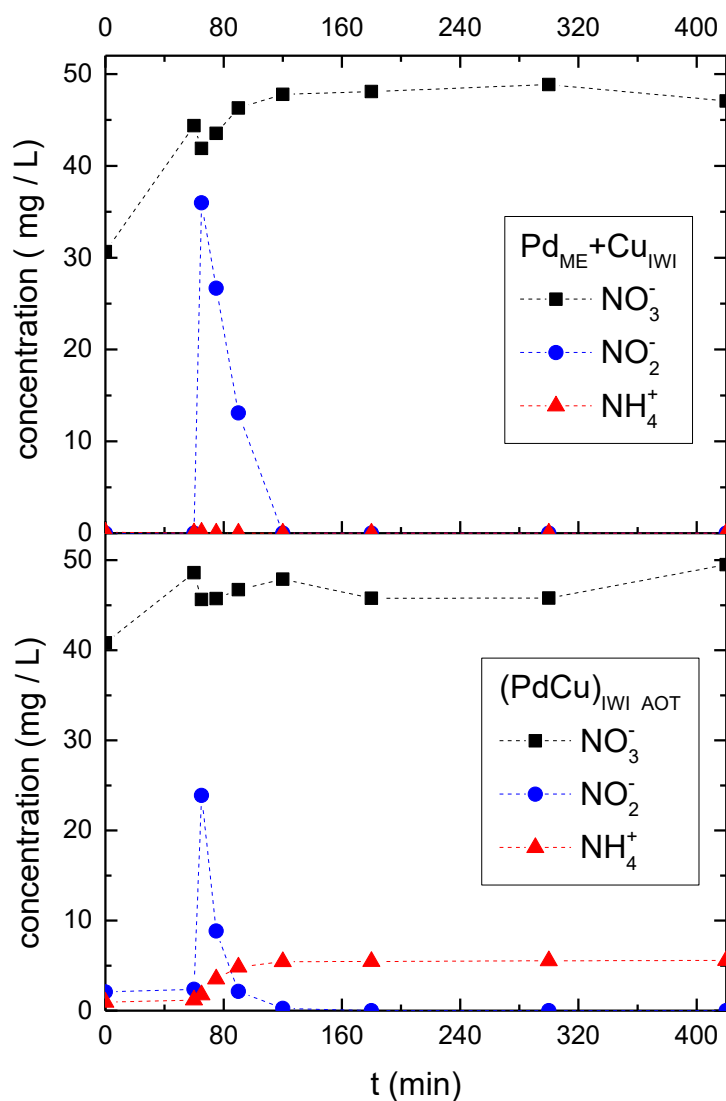


Figure 7. Time course of NO_3^- , NO_2^- and NH_4^+ in the simultaneous NO_3^- and NO_2^- reduction tests with $\text{Pd}_{\text{ME}} + \text{Cu}_{\text{IWI}}$ and $(\text{PdCu})_{\text{IWI AOT}}$ catalysts. $[\text{NO}_3^-]_0 = 50 \text{ mg / L}$; 50 mg/L of NO_2^- was added at $t = 60 \text{ min}$.

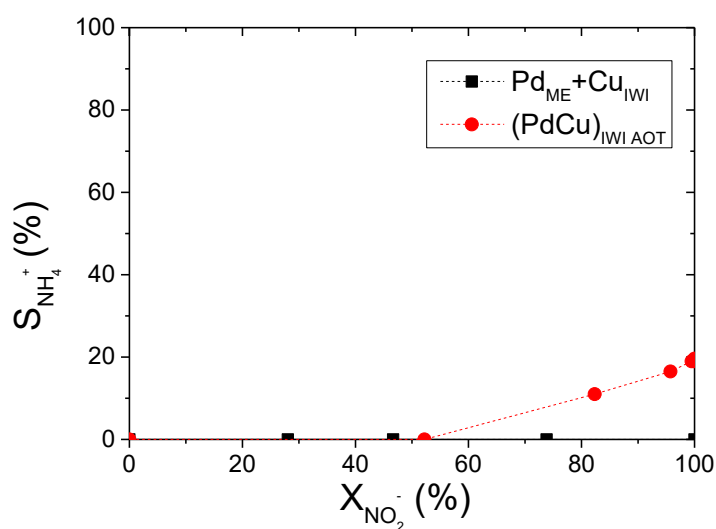


Figure 8. Selectivity to NH_4^+ versus NO_2^- conversion in simultaneous NO_3^- and NO_2^- reduction tests with $Pd_{ME}+Cu_{IWI}$ and $(PdCu)_{IWI AOT}$ catalysts.

Figure 9. depicts the reaction scheme reported by Martinez et al. (2017), including the steps in nitrate reduction which could be hindered by AOT, which also could limit hydrogen spillover. This would impede completing the redox cycle, thus contributing to lower accumulation of hydrogenated species on the catalyst surface and preventing the ammonium formation.

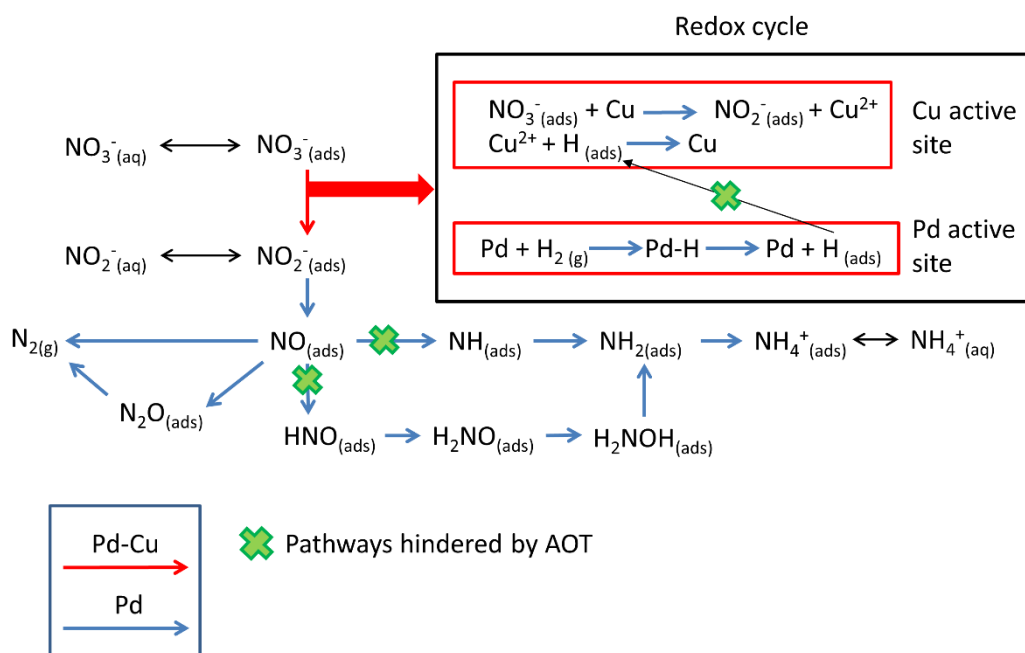


Figure 9. Reaction scheme of catalytic nitrate reduction including the pathways hindered by AOT.

The novel catalysts described in the current work can be prepared using scalable synthesis methods and affordable reagents and supports, thus avoiding bottlenecks in demonstration and large scale application. Likewise, the availability of granular activated carbons facilitates the use of the catalysts in trickle bed already used for nitrate reduction at bench scale, which is a common option in commercial gas-liquid-solid catalytic reactors.

4. Conclusions

Shielding of PdCu active sites with AOT in the synthesis of a variety of bimetallic PdCu catalysts was successfully applied to improve the control of ammonium formation in

1 the chemical reduction of nitrate. Pd-AOT interaction achieved due to microemulsion
2 synthesis or to exposure to AOT of IWI catalysts provoked a decrease in the activity for
3 nitrate reduction, both of bimetallic and PMMC. This loss of activity can be mostly
4 ascribed to interference of AOT in the Pd-Cu redox mechanism probably by limiting
5 hydrogen spillover. However, shielding by AOT prevented successfully the generation
6 of ammonium and complete selectivity to nitrogen was observed in some cases. The
7 tests for the simultaneous reduction of nitrate and nitrite with selected catalysts
8 showed that in spite of the loss of activity in nitrate reduction the catalysts maintain
9 the ability for nitrite reduction (100% conversion) with negligible ammonium
10 formation. Therefore, shielding of Pd active sites by AOT during catalyst synthesis
11 provides an effective way to avoid or significantly decrease ammonium formation in
12 nitrate reduction. However, more research is required to achieve a better balance
13 between activity in nitrate reduction and selectivity to ammonium.”
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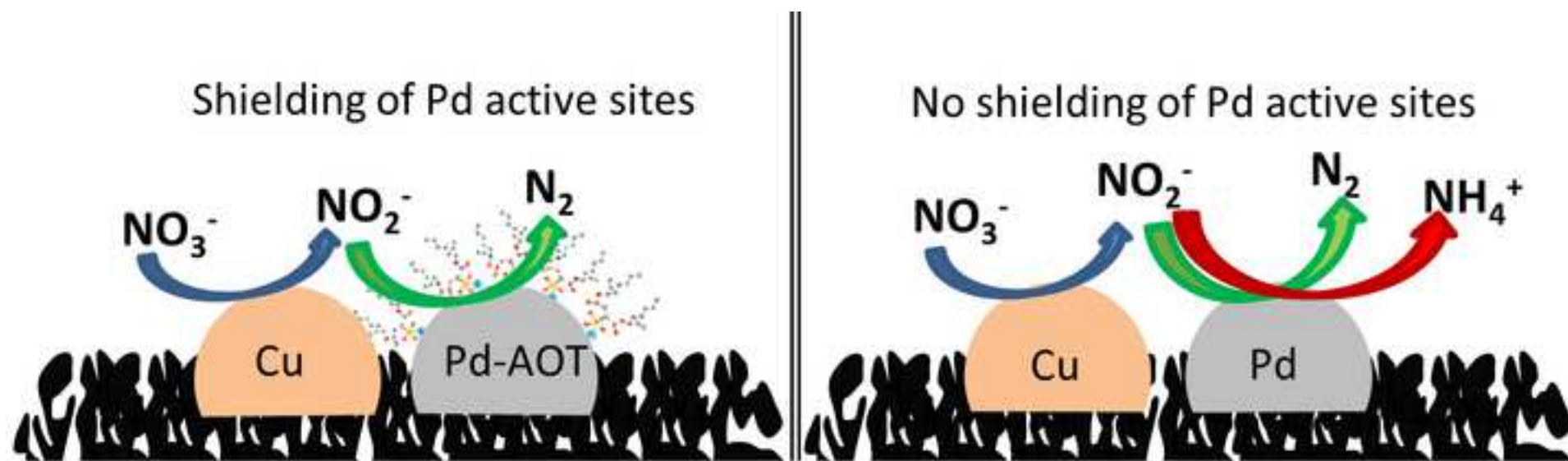
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Highlights

A new approach to control NH_4^+ formation in nitrate reduction was effectively proven

The shielding of active sites by AOT in Pd-Cu/C catalysts avoided the NH_4^+ formation

The Pd-AOT interaction provoked a decrease in the activity for nitrate reduction

The interference of AOT in the Pd-Cu redox mechanism could led to decreased activity