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REMOVAL OF NITRATE FROM DRINKING WATER BY USING PdCu STRUCTURED CATALYSTS BASED ON CORDIERITE MONOLITHS

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Abstract - Structured catalysts were prepared, characterized and evaluated in NO_3^- removal from drinking water. Different suspensions containing a previously optimized PdCu/5wt% ZrO_2-Al_2O_3 powder catalyst (hereinafter PdCu/5ZA_p) were prepared and deposited on cordierite monoliths by washcoating. The effect of suspension concentration, the particle size, the immersion number, the use of suspension stabilizer agent, and an alumina pre-coating on the coating adherence and catalytic performance were studied. All the prepared structured catalysts were active for the elimination of NO_3^- and presented good selectivity to N_2 (> 93%) in synthetic water samples. The catalyst performance was related to the amount of deposited catalyst. The highest activity and the best coating adherence were obtained with the structured catalyst prepared by a single immersion in a 14 wt% concentration suspension, which was obtained from the powder catalyst milled for 10 h and stabilized with colloidal alumina. This catalyst also showed good activity when it was reused for four cycles and when it was evaluated with real water samples.

Keywords: Water pollution; Nitrate; Cordierite monoliths; PdCu catalyst; Structured catalyst.

INTRODUCTION

Industrial and agricultural activities lead to the discharge of pesticides, fertilizers and organic wastes of animals and plants that contaminate the water in a diffuse but very remarkable way, in particular, groundwater. One of the most serious problems is the high levels of nitrate (NO_3^-) found in some groundwater reservoirs (Faridullah et al., 2017 ; Xu et al., 2017). When NO_3^- levels in soil are greater than the ones plants can assimilate, irrigation and rainwater cause NO_3^- to percolate and reach the groundwater. This fact affects the quality of life and health of a significant number of people, especially in areas dominated by agricultural activities (Zhai et al., 2017). Drinking water with excess NO_3^- ion can be harmful because NO_3^- is easily reduced to nitrite (NO_2^-) in the mouth and intestines, causing methemoglobinemia, a conversion of hemoglobin to methemoglobin that depletes oxygen levels, particularly in children under 6 months (blue-baby syndrome). In addition, NO_3^- is a precursor of carcinogenic nitrosamines (Zhai et al., 2017). The maximum contaminant level permitted by the US Environmental Protection Agency (EPA) is 10 ppm for N-NO_3^- (expressed in terms of nitrogen N in NO_3^-) in the water supply for the population (water.epa.gov/drink/contaminants/basicinformation/nitrate.cfm) .While for the World Health Organization (WHO) it is 50 ppm for NO_3^- and 1 ppm for NO_2^- (www.who.int/water_sanitation_health/dwq/chemicals/nitratenitrite2ndadd.pdf).

In Argentina, the Argentine Food Code establishes a maximum concentration of 45 ppm for NO_3^- and 0.1 ppm for NO_2^-(www.anmat.gov.ar/alimentos/normativas_alimentos_caa.asp).

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There are different treatments for NO_3^- removal from water such as electrodialysis, distillation, ion exchange, reverse osmosis, catalytic or electrochemical reduction, biological degradation, among others (Li et al., 2017; Huo et al., 2017). For environmental reasons, the best technique to remove NO_3^- should convert it to gaseous N_2. One of the most promising processes is the reduction of NO_3^- to N_2 using heterogeneous catalysts in the presence of H_2 as a reducing agent (Huo et al., 2017; Mirabi et al., 2017). These catalysts generally contain a noble metal (Pd, Rh, Ru or Pt) and a promoter metal (Cu, Ag, Fe, Hg, Ni, Cu, Zn, Sn or In) (Ding et al., 2017; Zoppas et al., 2016; Kim et al., 2016; Martínez et al., 2017). In these catalysts, the bimetallic sites permit the reduction of NO_3^- to NO_2^-, which is then reduced to N_2 or over-reduced to NH_4^+ over the monometallic sites. This latter product is an inconvenient aspect of these systems (Hamid et al., 2018; Martínez et al., 2017).

The powder catalysts containing PdCu or RhMo as active phase supported on Al_2O_3 or ZrO_2, both pure and mixtures of these supports, were previously evaluated in our group. These catalysts showed good catalytic performance in a batch reactor (Jaworski, et al., 2014; 2018). Particularly, it was found that the PdCu catalyst supported on ZrO_2-Al_2O_3 showed good catalytic activity and N_2 selectivity (Jaworski, et al., 2014). Despite the good activity and selectivity results obtained with these catalysts in a batch reactor, the use of a catalyst in a powder form is not technologically viable. The use of these catalysts could cause problems in their recovery, leading to the contamination of the treated water by metal particles. To avoid the loss of catalytic material, the use of pellets or extruded supports is proposed. A disadvantage of the use of pellets is that the diffusion of reagents and/or products into the pores of the catalysts would decrease the selectivity to N_2 (Durkin et al., 2018; Zoppas et al., 2018).

The use of structured catalysts such as monoliths, foams and grids could overcome the limitations caused by the use of powder formulations (Durkin et al., 2018; Li et al. 2019; Muñoz-Murillo et al., 2018). Structured catalysts based on monoliths with different chemical composition are widely used, especially in environmental catalytic applications. For example, Ni-based catalysts (Ni-CeO_2) prepared on ceramic monoliths have been obtained by dip-coating the support in an acid-free stable catalyst dispersion. The structured catalysts obtained were evaluated towards the biogas oxy-steam reforming reaction. The use of structured system instead of packed bed reactors allows one to obtain stable performances, in term of CH_4 (97%) and CO_2 (87%) conversion (Balzarotti et al., 2018).

Some of the structured catalysts used are supported on ceramic monoliths. These monoliths contain parallel channels of an inert oxide such as cordierite ($2MgO_2.Al_2O_3.5SiO_2$) and are coated with a thin layer of the catalyst (Özyönüm et al., 2016; Şem et al., 2016). Cordierite has numerous important applications due to its low cost, its excellent properties, such as low coefficient of thermal expansion, good thermal resistance, low dielectric constant, high chemical inertness, refractoriness and adequate mechanical properties (Labhsetwar et al., 2012; Yuan et al., 2016).

A series of copper/ceria washcoated cordierite monoliths was prepared and tested in the carbon monoxide preferential oxidation reaction. These catalysts were active in the CO-PROX reaction and CO-PROX stage, and could be used in the case of non-stationary applications (Landi et al., 2016). Volatile organic compounds (VOCs) that are air pollutants released from many industrial operations were eliminated using a honeycomb monolith washcoated with Mn-M mixed oxide (M= Cu, Ni or Co) (Zhang and Wu, 2016) or by using Mn, Ce and Ce/Mn supported ceramic monoliths with natural clays as raw materials (Colman-Lerner et al., 2016). Catalysts of $LaCoO_3$/ɤ-Al_2O_3/cordierite monolith, $LaCoO_3$/SiO_2/cordierite monolith and $LaCoO_3$/TiO_2/cordierite monolith were used to reduce diesel particulate emissions that cause serious problems in human health (Tang et al., 2017).

Considering the advantages of the structured catalysts, in this work the preparation of cordierite monoliths coated with a powder catalyst previously optimized by our group is reported. The powder catalyst is PdCu supported on Al_2O_3 modified with 5 wt% ZrO_2 (PdCu/5ZA_P), which showed good catalytic performance in the NO_3^- removal reaction (Jaworski, et al., 2014).

It has been shown that the adherence of the active phase to the monolith is essential in the development of structured catalysts (Ashraf et al., 2018; Sedjame et al., 2018). Different factors affect this adherence, such as the characteristics of the suspension containing the active phase, the particle size of the solid to be deposited on the monolith, the nature of the dispersion medium, the concentration of solids and pH of the suspension (Landi et al., 2016). For this reason, different suspensions of PdCu/5ZA_P were used for the washcoating of cordierite monoliths. The effects of the particle size, the solid concentration in the suspension, the addition of a suspension stabilizer, the number of immersions and the effect of a precoating on the adherence were studied. Furthermore, the catalytic performance for nitrate reduction in water was evaluated.

MATERIALS AND METHODS

Preparation of PdCu/5ZA catalyst

The synthesis and characterization of the PdCu/5ZA_P catalyst employed in this work were previously described (Jaworski et al., 2014). Briefly, in order to prepare the Al_2O_3 support modified with 5 wt% ZrO_2, $ZrOCl_2.6H_2O$ (Fluka) was added to the γ-Al_2O_3 support (γ-Al_2O_3 Air Products, surface area 190 m^2g^{-1}; pore volume 0.50 m^3g^{-1}) suspended in distilled water. NH_4OH was added drop by drop under constant stirring until a gel formed. This system was aged for 8 days. The solid obtained was washed until no chloride ion was determined by $AgNO_3$ solution, dried at 105°C and calcined at 400ºC for 2 h. The support obtained was called 5ZA. The Pd-based catalyst (1 wt%) was prepared by impregnating the 5ZA support with a solution of H_2PdCl_4 prepared from $PdCl_2$ (Sigma-Aldrich) in HCl (pH=1). The solid obtained was dried at 105ºC and calcined in air at 400°C. After that, this monometallic catalyst was impregnated with a solution of $Cu(NO_3)_2$ (Merck), so as to obtain 0.3 wt% Cu on the support. The bimetallic catalyst was first dried at 105ºC and then calcined at 400°C.

Preparation of cordierite monoliths

The structured support used was ceramic cordierite monoliths (Corning). They were sectioned in a suitable size (length: 3 cm, cross section: 0.785 cm^2), placed in an ultrasonic water bath to remove possible impurities, dried, weighed and identified. The scheme of the monoliths used is shown in Figure 1.

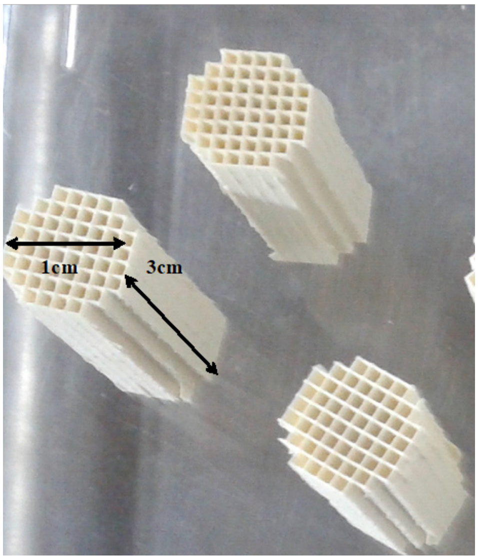

Figure 1. Scheme of the monoliths used.

The catalyst was incorporated into the monolithic structure using the washcoating method. This method consists of immersing the monolith in a suspension of the finely milled catalyst. In order to prepare a stable suspension, it was necessary to determine the zeta potential (pZ) of the PdCu/$5ZA_P$ catalyst. For this determination, the PdCu/$5ZA_P$ catalyst was milled to a particle size between 120 and 140 mesh. The determination of the pZ was carried out with solutions of KCl, KOH and HCl using Zeta-Meter System 3.0 equipment.

For the preparation of the PdCu/$5ZA_P$ suspension, the catalyst was finely milled for 5 or 10 h in a planetary ball mill (Fritsch Pulverisette 6). The particle size of the PdCu/$5ZrAl_P$ catalyst after milling was determined using a Fritsch A-20 photosedimentograph and 2% Triton X-10 as surfactant.

Preparation of the structured catalysts

In order to obtain a stable coating of the PdCu/$5ZA_P$ catalyst on the monolith structure, different preparation strategies were evaluated. For example, the effect of the milling time for the PdCu/$5ZA_P$ catalyst (5 or 10 h), the catalyst concentration in the suspension (14 or 20 wt%), the stabilizer agent (colloidal alumina Nyacol® Al 20 or polyvinyl alcohol (PVA)) and the precoating of monoliths with colloidal alumina Nyacol® Al 20 as primer were studied.

To prepare the structured catalyst, an aqueous suspension of the finely milled PdCu/$5ZA_P$ catalyst was prepared and the pH was adjusted to 9.5 with a concentrated NaOH solution. The suspension obtained was placed in an ultrasound device for 30 min and its stability was observed. The cordierite monoliths were immersed in this suspension for 1 min. The excess suspension was eliminated by centrifugation at 650 rpm for 1 min. Finally, the monoliths containing the deposited catalyst were dried at 105ºC, calcined at 400°C for 2 h and weighed.

The monolithic catalysts prepared are listed in Table 1, where N or P indicates the Nyacol® Al 20 or PVA stabilizer, respectively, 14 or 20 is the weight percentage of the catalyst in the suspension, 5 or 10 indicates the powder catalyst milling time, Pr indicates the precoating with colloidal alumina Nyacol® Al 20 as primer, and (1) or (2) is the number of monolith

Table 1. Nomenclature and methodologies employed to deposit the PdCu/$5ZA_P$ catalyst on monoliths.

Monolith	Milling time (h)	Pre-coating	Stabilizer	Suspension concentration (wt.%)	Number of immersions
N20-5(1)	5	No	Nyacol	20	1
N14-5(1)	5	No	Nyacol	14	1
N14-5(2)	5	No	Nyacol	14	2
N14-10(1)	10	No	Nyacol	14	1
N14-10 Pr(1)	10	Yes	Nyacol	14	1
P14-10(1)	10	No	PVA	14	1
P14-10 Pr(1)	10	Yes	PVA	14	1

dips in the suspension. Four pieces were prepared for each condition to verify the reproducibility of the preparation method.

Adherence test

In order to evaluate the coating adherence of the PdCu/5ZA$_p$ catalyst on the monoliths, an adaptation of a previously reported method (Barbero, et al., 2008) was used. The structured catalysts were immersed in distilled water inside a sealed beaker and subjected to ultrasonic agitation at approximately 30 °C for 30 min. Then, the structured catalysts were dried at 105 °C for 6 h and calcined at 400 °C for 2 h. These conditions are identical to that employed during the washcoating of PdCu/5ZA$_p$ catalyst. Therefore, the weight difference before and after the ultrasound treatment allows one to determine the coating adherence as following:

$$\text{Adherence}(\%)=\left[1-\frac{(W_{bu}-W_{au})}{W_{cat}}\right]\times 10 \qquad (1)$$

where W_{bu} is the weight before ultrasonic treatment, W_{au} the weight after ultrasonic treatment, and W_{ap} the weight of PdCu/5ZA$_p$ catalyst retained by washcoating.

Characterization of PdCu/5ZA structured catalysts

Monolithic catalysts were characterized by SEM-EDX microscopy. SEM-EDX measurements were carried out using a FEI Quanta 200 scanning electron microscope equipped with an energy dispersive X-ray spectroscopy facility (EDX SDD Apollo 40). In order to draw conclusions about the distribution of the components in the samples, backscattered electron (BSE) images were taken.

The temperature-programmed reduction (TPR) experiments were carried out in a conventional flow system using a reactive gas stream (5% H_2 balanced with Ar) flowing at 25 mL min^{-1} over 50 mg of sample. The temperature was raised from room temperature to 800 °C at 10 °C min^{-1}. Hydrogen uptake during the reduction was analysed on-line by a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector (TCD).

The textural properties of the supports were measured by N_2 adsorption-desorption at −196 °C using a Micromeritics Accusorb 2100E apparatus.

Analysis of the catalytic properties

A tubular glass reactor (internal diameter: 1.1 cm; length: 3.1 cm) containing the structured catalysts (Figure 2) was used to study NO_3^- removal from water. Fifty mL of degassed aqueous solution containing 100 ppm of NO_3^- was loaded into the system and continuously bubbled with H_2. The solution was recirculated with a peristaltic pump at a flow rate of 5 mL/min. The reaction was carried out for 20 h at room temperature and atmospheric pressure.

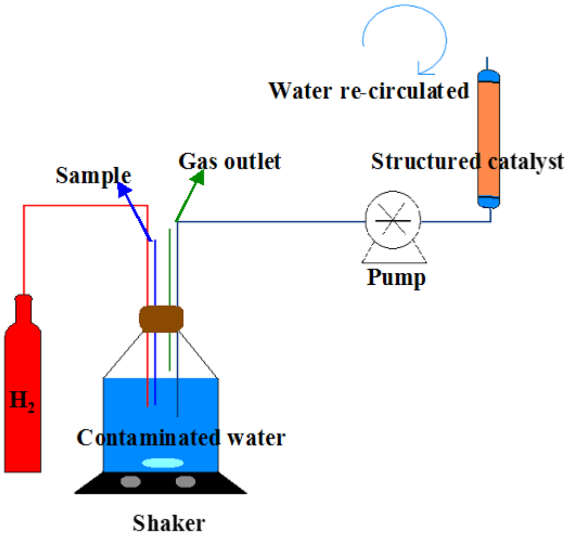

Figure 2. Schematic diagram of the experimental equipment.

Samples were periodically taken to determine NO_3^- and NO_2^- concentration with an ion chromatograph (Metrohm 790 Personal IC). NH_4^+ was determined at the end of the reaction by a colorimetric method using a UV-Vis spectrophotometer (UV-Vis Thermo Spectronic Helios Gamma), following a modified Berthelot method (Marchesini et al., 2010). The conversion values of NO_3^- (X_{NO3-}%) as well as selectivities towards NO_2^- (S_{NO2-}%), NH_4^+ (S_{NH4+}%) and N_2 (S_{N2}%) after 20 h of reaction for all the catalysts studied were calculated according to:

$$X_{NO_3^-}=\frac{\left[NO_3^-\right]_{initial}-\left[NO_3^-\right]_t}{\left[NO_3^-\right]_{initial}}\times 100\% \qquad (2)$$

$$S_{NO_2^-}=\frac{\left[NO_2^-\right]_t}{\left[NO_3^-\right]_{initial}-\left[NO_3^-\right]_t}\times 100\% \qquad (3)$$

$$S_{NH_4^+}=\frac{\left[NH_4^+\right]_t}{\left[NO_3^-\right]_{initial}-\left[NO_3^-\right]_t}\times 100\% \qquad (4)$$

$$S_{N_2}=100-S_{NO_2^-}(\%)-S_{NH_4^+}(\%) \qquad (5)$$

RESULTS

Characterization of the structured catalysts

The uncoated monolith and the structured catalysts were analysed by SEM-EDX microscopy. A representative SEM-EDX analysis of a portion of the

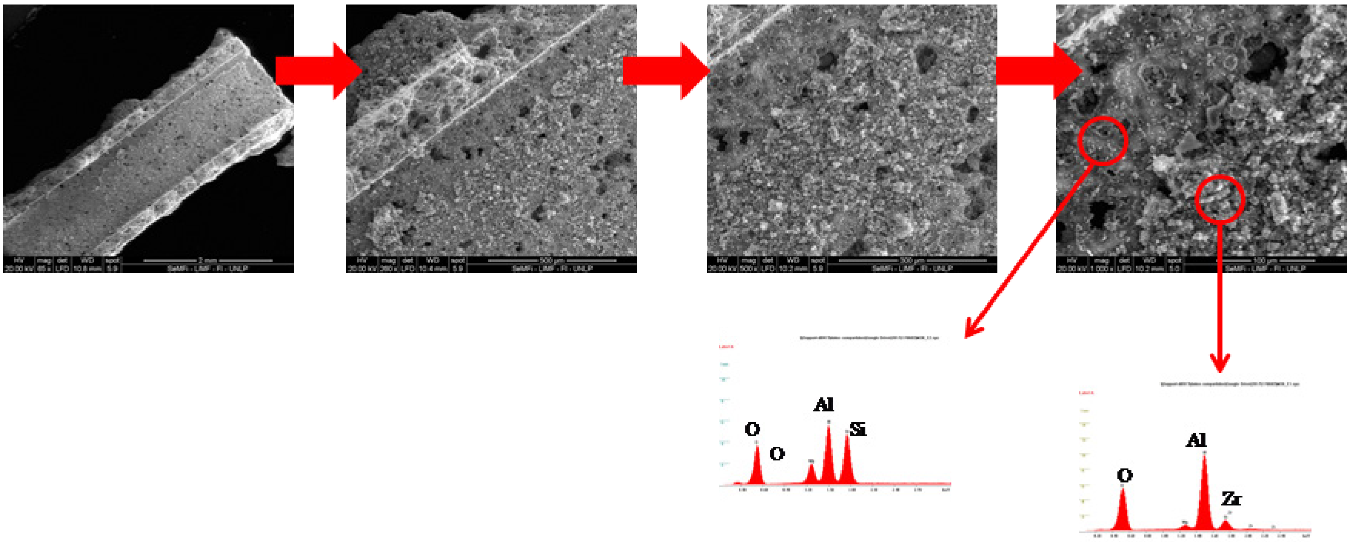

Figure 3. SEM image and EDX analysis for the structured catalyst N14-10(1).

catalyst N14-10(1) is shown in Figure 3. The arrows indicate a progressive increase of zoom for the images. The circles indicate the points where the elements were analysed by EDX.

The areas of the monolith covered with catalyst were clearly distinguished in all the analysed monoliths. The EDX analysis of the uncovered areas showed the presence of O, Mg, Al and Si, representative of cordierite, while the areas with the catalyst presented O, Al and Zr, which indicates the effective coating of the PdCu/5ZA$_P$ catalyst on the monolith surface. As expected, it was not possible to differentiate the metals Pd and Cu because they are in concentrations below the detection limit of EDX.

To determine if the catalyst particles were modified during the washcoating process, the textural properties (Figure 4) and the TPR profile (Figure 5) of the original PdCu/5ZA$_P$ catalyst were compared with those of the

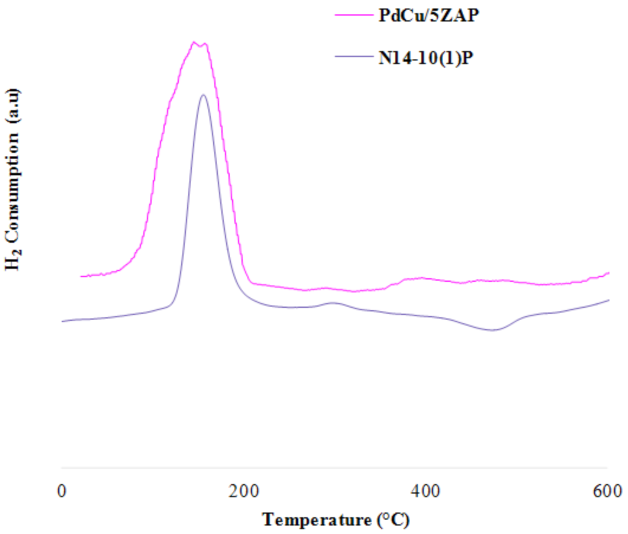

Figure 5. TPR profile of the catalyst PdCu/5ZA$_P$ and N14-10(1)$_P$.

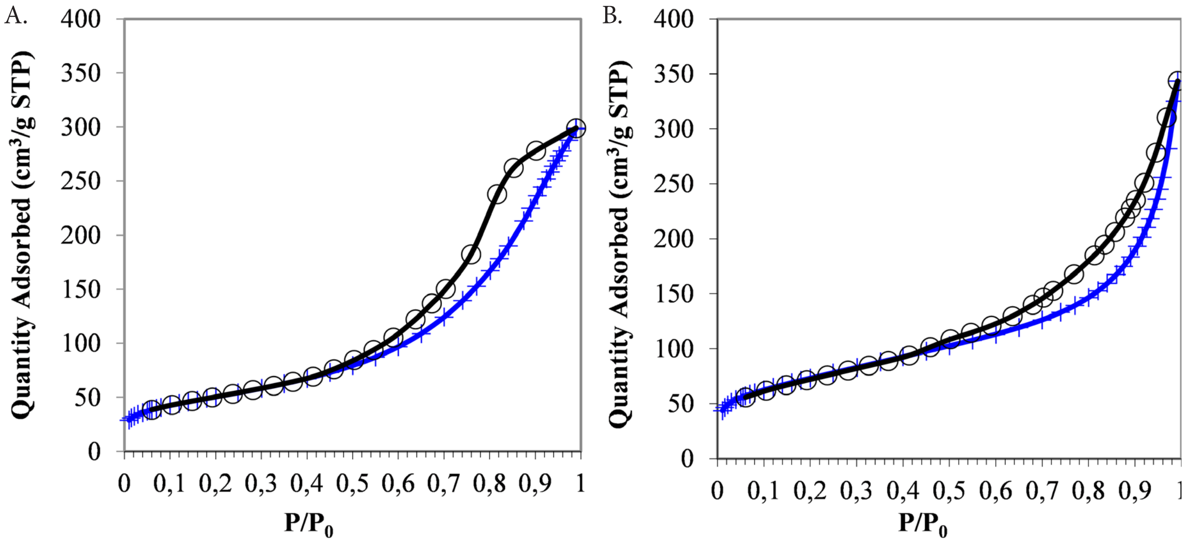

Figure 4. N_2 adsorption/desorption isotherms at for a) PdCu/5ZA$_P$, b) N14-10(1)$_P$.

solid recovered by drying of the suspension used to prepare monolith N14-10(1) (hereinafter called N14-10(1)$_P$).

The N_2 adsorption/desorption isotherms for the powder catalyst PdCu/5ZA$_P$ and N14-10(1)$_P$ are shown in Figure 4 a) and b), respectively. The catalytic materials analysed have similar isotherms corresponding to a type IV isotherm according to the IUPAC classification, characteristic of mesoporous solids (Muttakin et al., 2018).

The TPR profile for the catalyst PdCu/5ZA$_P$ was described in a previous paper (Jaworski, et al., 2014) and was similar for the solid N14-10(1)$_P$, Figure 5. In both profiles it is possible to distinguish two different peaks: a main peak centred around 150ºC and a small peak which extends between 300 and 400ºC. The first peak is assigned to the reduction of PdO to Pd^0, and the reduction of copper oxides promoted by the presence of the noble metal Pd (Resende et al., 2018, Zhuang, et al., 2010).The Pd crystals favor the spillover of H_2 that causes the Cu oxides to be reduced at lower temperature when compared to a monometallic Cu catalyst (300-400°C) (Lei et al. 2018; Yuan et al., 2017). The second peak corresponds to the reduction of CuO to Cu^o (Lei et al., 2018).

The similarity of the TPR profiles for the catalysts PdCu/5ZA$_P$ and N14-10(1)$_P$ show that the Pd-Cu interaction is not modified when the catalyst is finely milled and used for preparing the suspension.

Determination of the isoelectric point

As previously mentioned, it was necessary to determine the pZ of the PdCu/5ZA$_P$ catalyst prior to preparing the suspensions. In Figure 6 it can be seen that the isoelectric point for the PdCu/5ZA$_P$ catalyst was approximately 4.5. Then, the pH selected to prepare the PdCu/5ZA$_P$ catalyst suspension was 9.5, which is far enough away from pZ. In this way, the agglomeration of particles was avoided.

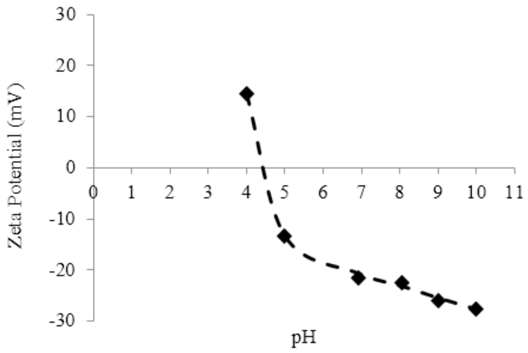

Figure 6. Zeta potential as a function of pH for the PdCu/5ZA$_P$ catalyst.

Determination of particle size

Figure 7 shows the curves corresponding to the determination of the particle size distribution after the milling process (5 h and 10 h).

The continuous line with square symbols represents the particle size distribution, while the dashed line with triangle symbols represents the accumulative distribution. From these curves it is possible to read the d_{50} or d_{90} (50% or 90% of the particles of the suspension are smaller than that value, respectively). For the milling time of 5 h, d_{90} of 25.5 µm was obtained. For the10 h milling time, the d_{50} was 7 µm and the d_{90} 13.5 µm approximately. Evidently, the particle sizes for 5 h milling time are larger than for 10 h milling time.

Results of coated monoliths

Table 2 presents the catalyst mass gained by washcoating and the coating adherence for all prepared monoliths. The second column shows the weight increase observed after washcoating of the cordierite monolith, which correspond to the content of PdCu/5ZA$_P$ catalyst on the cordierite support expressed as weight percentage. The values reported are an average of the four pieces prepared. The third column shows the percentage of PdCu/5ZA catalyst

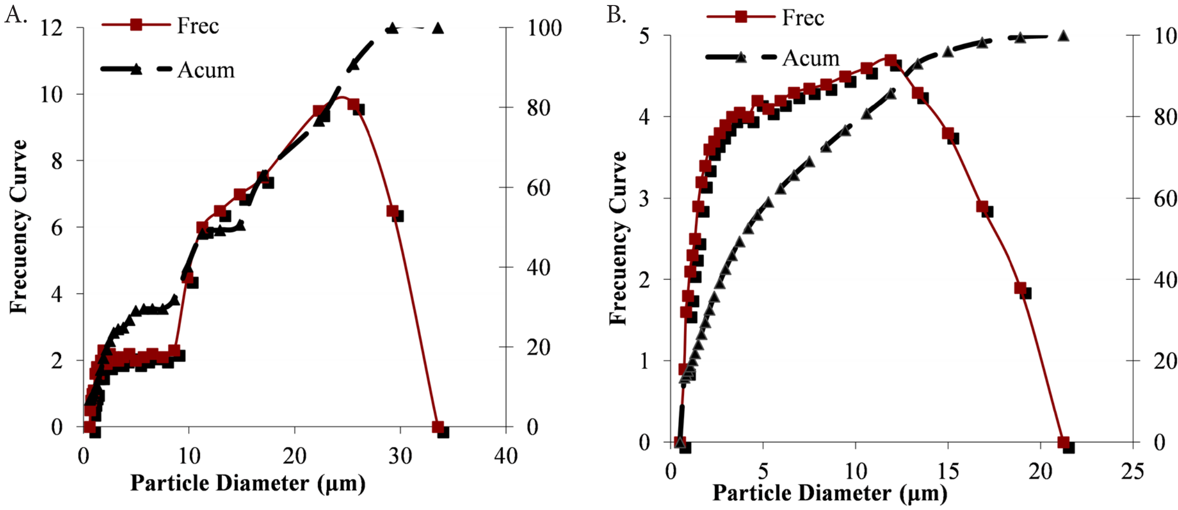

Figure 7. Determination of the particle size after the milling process. Left, 5 h milling. Right, 10 h milling.

Table 2. Weight percentage of PdCu/5ZA$_P$ catalysts retained after the washcoating (second column), coating adherence (third column) and net content of PdCu/5ZA$_P$ catalyst after the adherence test (fourth column).

Monolith	Weight increase (wt%)	Adherence (%)	Catalyst net content (wt%)
N20-5(1)	4.79±0.03	48.57	2.33
N14-5(1)	4.35±0.02	66.67	2.90
N14-5(2)	8.45±0.01	40.00	3.38
N14-10(1)	3.33±0.02	90.00	3.00
N14-10 Pr(1)	4.55±0.02	61.67	2.80
P14-10(1)	2.05±0.01	83.33	1.71
P14-10 Pr(1)	2.88±0.02	75.00	2.16

retained after the adherence test with respect to the catalyst retained by the washcoating process. The net content of catalyst after the adherence test is shown in the last column. These results are discussed below.

Effect of suspension concentration

The structured catalyst prepared using the 20 wt% suspension (N20-5(1)) showed a non-uniform coverage and channels blocked by the active phase.

To avoid these problems and to obtain a homogeneous layer of the catalyst on the monolith, a more dilute suspension, 14 wt%, was used (monolith N14-5(1)). The monoliths were coated with this suspension and Table 2 (second column) shows that the mass gain of catalyst is smaller for N20-5(1) than for N14-5(1) monolith. A better adherence (third column) is achieved when the 14 wt% suspension in used. In this way, higher catalyst net content is obtained after the adherence test (fourth column).

Effect of the number of immersions

To increase the amount of catalyst in the monoliths, two immersions were made with the 14 wt% suspension, obtaining N14-5(2) monolith. From Table 2 it is noted that, with two immersions, about the double of catalyst was retained on the monolith (second column). However, a significant amount of catalyst was not retained after the adherence test for this monolith. As was previously reported, it is possible that, with a greater number of immersions, an unstable coating will be formed on the monolith (Bosko et al., 2014). The attraction forces between the first and the second layers deposited on the monolith are weak. Therefore, the coating adherence decreases for subsequent immersions.

Effect of catalyst particle size

In order to analyse the effect of the catalyst particle size, the PdCu/ZA$_P$ catalyst was milled for 5 or 10 h (Figure 7) and two monoliths were prepared (monolith N14-5(1) and N14-10(1)). In Table 2, it can be seen that the milling time affected the final adherence of the catalyst. The monolith coated with the powder milled for 10 h was more stable than that coated with the powder milled for 5 h. This implies that the small particle size favours the adherence of the coating.

Effect of the stabilizer agent

Alternatively to the use of colloidal alumina Nyacol® Al 20 as the stabilizer agent of the suspension, PVA was used and the monolith P14-10(1) was prepared. In comparison with the monolith N14-10(1), the monolith prepared with PVA retained less catalyst amount and presented lower coating adherence (Table 2).

Effect of the use of a primer

The adherence of the catalyst to the monolith is a crucial factor. For this reason, to improve adherence, usually the monolith is firstly covered with a layer of alumina or silica oxides. The function of these oxides is to provide a bond between the catalyst particles and the monolith, without affecting the catalytic performance (Yuan et al., 2016). In this work, the cordierite monoliths were immersed in a suspension of colloidal alumina Nyacol® Al20 for 1 min. The excess of the suspension was removed by centrifugation at 650 rpm for 1 min. The monoliths containing the primer were dried, calcined at 500 °C for 2 h and weighed. The PdCu/5ZA$_P$ powder catalyst (14 wt% suspension) milled for 10 h was then deposited on these monoliths. Two suspensions were made using the stabilizers previously evaluated, colloidal alumina or PVA, and the monoliths obtained were N14-10 Pr(1) and P14-10 Pr(1).

By comparing the monoliths without primer (N14-10(1) and P14-10(1)) with the monoliths with primer (N14-10 Pr(1) and P14-10 Pr(1)), it can be seen that the use of a primer was not favourable (Table 2). The amount of catalyst retained was higher compared to the same monoliths containing no primer (Table 2, second column) but the adherence of these coatings was lower (Table 2, third column). It was suggested that the presence of a primer could cause the loss of the surface roughness of the monolithic support and, for that reason, the adherence decreases (Yuan et al., 2016).

Catalytic reaction

Before testing the monolithic catalysts in the NO_3^- removal reaction in water, blank tests were performed. The first one consisted of the use of 50 mL of a 100 ppm NO_3^- solution in the presence of H_2 bubbling but in the absence of catalyst. The second one consisted in the use of the structured support covered by powder Al_2O_3 or 5ZA supports in the presence of 100 ppm of NO_3^- and H_2. In both cases, it was found that NO_3^- removal was null.

All PdCu/5ZA monolithic catalysts were evaluated in the NO_3^- removal reaction. The PdCu/5ZA$_P$ powder catalyst was included as a reference. The results are shown in Table 3.

This study showed that the structured catalysts prepared were active in the removal of NO_3^-. A maximum conversion of 83% after 20 h of reaction was found for the monolith N14-10(1). This monolith also had the best N_2 selectivity and the highest nitrate specific conversion (calculated as (nitrate conversion)/(catalyst mass) ratio, Table 3, eighth column). For all the monoliths studied, the selectivity to N_2 was higher than 96%, except for the monolith N20-5(1). These results make these systems promising candidates to be used as catalysts for NO_3^- removal from water, although some operation conditions could still be improved.

In order to evaluate the existence of diffusional effects on NO_3^- removal, another test was carried out using an aliquot of the PdCu/5ZA$_P$ powder catalyst obtained from the suspension used to prepare the catalyst N14-10(1). The reaction was carried out in a semibatch system using 45 mg of this powder, which is equal to the catalyst mass retained on the monolith N14-10(1). The reaction conditions were the same as in the previous tests. The final concentrations detected for NO_3^-, NO_2^- and NH_4^+ were 0 ppm, 0.5 ppm and 0.3 ppm, respectively. The difference in activity between the powder and the monolith N14-10(1) could be assigned to diffusion problems of the reactants and/or products in the structured system.

In summary, from the results shown in Tables 2 and 3, the preparation of structured catalysts using the catalyst PdCu/5ZA$_P$ milled for 10 h in the absence of a primer is favourable since the best results in terms of catalyst retention and catalytic activity were obtained using the N14-10(1) monolith.

As previously mentioned, in the blank tests using the cordierite monolith covered with the supports Al_2O_3 or 5ZA, NO_3^- removal was null. Since the support itself is not active, the NO_3^- removal is attributed to the PdCu active phase. In this sense, the same reaction mechanism described by Jaworski et al. (2014) in a previous work is postulated. In this mechanism, the NO_3^- ions are adsorbed on the oxygen vacancy sites (Lewis acid sites) generated by the presence of ZrO_2 in the support.

In order to evaluate the potential reuse of the monolith N14-10(1), after reaction, the monolith was washed with distilled water, dried, calcined at 400°C for 1 h and reduced at 400°C for 1 h. The reaction was carried out using the original NO_3^- solution (100 ppm of NO_3^-). This process was repeated for each cycle. The results obtained are listed in Table 4.

The results from Table 4 show that there is a certain deactivation in the removal of NO_3^- after each reuse, while the selectivity to NO_2^- and NH_4^+ is maintained. The mass of the catalyst remains constant before and after each use. Thus, the decrease in activity for NO_3^- removal could be assigned to the loss of some of the active sites.

For these catalysts to have a practical application, it is necessary to evaluate them in water intended for human consumption. In this sense, the monolith with the best catalytic performance, N14-10(1), was evaluated using water samples taken from the Puelche Aquifer. Two samples of groundwater from this aquifer were extracted and analysed, and were designated C and P, as shown in Table 5. The nitrate content of these samples was higher than that allowed by current regulations. The Puelche Aquifer is one of the most exploited water reservoirs in Argentina, since it supplies drinking water to the Buenos Aires Metropolitan Region (Greater Buenos Aires), one of the most densely populated areas of Argentina. The Puelche Aquifer has low salinity (approximately 585 mg/L), being of the sodium bicarbonate type. Its potability is only affected by the NO_3^- content, especially in urbanized areas (Armengol et al., 2017; Zabala et al. 2016).

Table 4. Conversion of NO_3^- and concentration of NO_2^- and NH_4^+ after re-use of the N14-10(1) monolith.

Cycle	X_{NO3-}%	ppm NO_2^-	ppm NH_4^+	S_{NO2-} (%)	S_{NH4+} (%)	S_{N2} (%)
1°	83	0.4	0.55	0.48	0.66	98.86
2°	75	0.9	0.3	1.20	0.40	98.40
3°	68	0.75	0.3	1.10	0.44	98.46
4°	61	0.4	0.25	0.66	0.41	98.93

Table 3. Conversion of NO_3^- and concentration of NO_2^- and NH_4^+ for the monoliths prepared after 20 hours of reaction.

Monolith	X_{NO3-} (%)	ppm NO_2^-	ppm NH_4^+	S_{NO2-} (%)	S_{NH4+} (%)	S_{N2} (%)	X_{NO3-} /g_{cat} *
N20-5(1)	45	0.8	2	1.78	4.44	93.78	13.24
N14-5(1)	75	0.55	0.4	0.73	0.53	98.73	18.75
N14-5(2)	78	0.75	0.6	0.96	0.77	98.27	16.25
N14-10(1)	83	0.4	0.55	0.48	0.66	98.86	18.44
N14-10 Pr(1)	61	1.2	0.7	1.97	1.15	96.89	16.49
P14-10(1)	42	1.1	0.4	2.62	0.95	96.43	16.80
P14-10 Pr(1)	53	0.9	0.6	1.70	1.13	97.17	18.93
PdCu/5ZA poder	100	0.5	0.3	0.50	0.30	99.20	20.00

*Nitrate specific conversion calculated as nitrate conversion per catalyst gram.

Table 5. Elimination of NO_3^- from water for human consumption after 20 h of reaction using N14-10(1) monolith*.

Sample	$ppm_i^{(1)}$ NO_3^-	X_{NO3^-}%	$ppm_f^{(2)}$ NO_2^-	$ppm_f^{(2)}$ NH_4^+	S_{NO2^-} (%)	S_{NH4^+} (%)	S_{N2}%
C	63	49	3.3	0.8	10.64	2.58	86.78
P	58	48	2.9	0.65	10.71	2.32	86.97

* For experimental conditions, see the text. (1) ppm_i: initial concentration (mg/L). (2) ppm_f: final concentration (mg/L).

The denitrification reaction was carried out for 20 h using the N14-10(1) monolith and H_2 as reducing agent, following the same procedure described in the experimental section for the synthetic samples. The results obtained are presented in Table 5.

The evaluated N14-10(1) monolith was active in the removal of NO_3^- from real water samples, although a high production of NO_2^- and NH_4^+ was observed, compared to the results obtained when analysing synthetic samples (Table 3). It is suggested that the decrease in the activity and the selectivity towards N_2 is due to the masking of the active phase caused by the rest of the ions present in the real water samples, especially to the abundant presence of bicarbonate ions present in the Puelche Aquifer. It is well-established that bicarbonate ions present similar chemical properties to nitrate ions, and thus it can be expected that both anions would be adsorbed on the same catalytic sites. Therefore, the catalytic surface available for nitrate ions will be lower, and so will be the activity (Mendow et al., 2017).

CONCLUSIONS

Unsupported catalysts are used in numerous industrial processes; however, most of the catalysts used in environmental processes must be supported. In this work structured catalysts were satisfactorily prepared and evaluated in the NO_3^- removal reaction in water in the presence of H_2 as a reducing agent. The powder catalyst PdCu/5ZA_P was deposited on cordierite monoliths by washcoating. The influence of different variables in the preparation of the structured catalysts was analysed: suspension concentration, particle size, number of immersions, nature of the stabilizer and the use of primer. It was found that the use of a 14 wt% catalyst suspension is more favourable than a higher suspension concentration (20 wt%) in order to prevent blocking of the monolith channels. A milling time of 10 h (reduction of the particle size of the powder catalyst) improved the amount of catalyst deposited and the adherence of the coating.

The use of colloidal alumina Nyacol as the stabilizer agent was more favourable than the use of PVA to improve the adherence of the catalyst to the monolith. One second immersion increased the retained catalyst mass, but the adherence was low.

The monolith N14-10(1) showed the best catalytic performance among all structured catalysts tested. Though there would be diffusional limitations in the catalytic coating, it should be noted that the selectivity to nitrogen was higher than 97% and this value remained after the reuse of the catalyst, making it a very promising catalytic system.

This structured catalyst eliminated 50% of the NO_3^- present in samples of water for human consumption, but high NO_2^- and NH_4^+ generation was detected. Probably the ions present in real water masked the NO_3^- adsorption sites.

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