

Activity and Selectivity of Bimetallic Catalysts Based on SBA-15 for Nitrate Reduction in Water

Mouhamad Rachini^{1,2,3}, Mira Jaafar^{1,3*}, Nabil Tabaja^{1,3}, Sami Tlais⁴, Rasha Hamdan^{1,3}, Fatima Al Ali³, Ola Haidar^{3,5}, Ali Jaber^{3,6}, Mohammad Kassem², Eugene Bychkov², Lucette Tidahy⁷, Renaud Cousin⁷, Dorothée Dewaele⁸, Tayssir Hamieh^{1,9*}, Joumana Toufaily^{3*}

¹Laboratory of Materials, Catalysis, Environment and Analytical Methods (MCEMA), EDST, FS, Lebanese University, Hariri Campus, Hadath, Lebanon

²Université du Littoral Côte d'Opale (ULCO), LPCA, EA 4493, F-59140 Dunkerque, France

³Laboratory of Applied Studies for Sustainable Development and Renewable Energy (LEADDER), EDST, Lebanese University, Hariri Campus, Hadath, Lebanon

⁴College of Engineering and Technology, American University of the Middle East, Kuwait, Kuwait

⁵Department of Chemistry, American University of Beirut, Riad El-Solh, Beirut, Lebanon

⁶Laboratoire de Recherche et Développement des Médicaments et des Produits Naturels RDMPN, Faculty of Pharmacy, Lebanese University, Hariri Campus, Hadath, Lebanon

⁷Université du Littoral Côte d'Opale, UCEIV, Unité de Chimie Environnementale et Interactions sur le Vivant, EA 4492, SFR Condorcet FR CNRS 3417, Dunkerque, France

⁸Centre Commun de Mesures, Université du Littoral Côte d'Opale, Dunkerque, France

⁹Faculty of Science and Engineering, Maastricht University, Maastricht, The Netherlands

Email: *mira.jaafar@hotmail.fr, *t.hamieh@maastrichtuniversity.nl, *joumana.toufaily@ul.edu.lb

How to cite this paper: Rachini, M., Jaafar, M., Tabaja, N., Tlais, S., Hamdan, R., Al Ali, F., Haidar, O., Jaber, A., Kassem, M., Bychkov, E., Tidahy, L., Cousin, R., Dewaele, D., Hamieh, T. and Toufaily, J. (2023) Activity and Selectivity of Bimetallic Catalysts Based on SBA-15 for Nitrate Reduction in Water. *Materials Sciences and Applications*, 14, 78-93.

<https://doi.org/10.4236/msa.2023.142006>

Received: January 20, 2023

Accepted: February 17, 2023

Published: February 20, 2023

Copyright © 2023 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Nitrate from the application of nitrogen-based fertilizers in intensive agriculture is a notorious waste product, though it lacks cost-effective solutions for its removal from potential drinking water resources. Catalytic reduction appears to be a promising technique for converting nitrates to benign nitrogen gas. Mesoporous silica SBA-15 is a frequently used catalyst support that has large surface areas and highly ordered nanopores. In this work, mesoporous silica SBA-15 bimetallic catalysts for nitrate reduction were investigated. The catalyst was optimized for the selection of promoter metal (Sn and Cu), noble metal (Pd and Pt) and loading ratios of these metals at different temperatures and reduction conditions. The catalysts prepared were characterized by FT-IR, N₂ physisorption, XRD, SEM, and ICP. All catalysts showed the presence of cylindrical mesoporous channels and uniform pore structures that remained even after metals loading. In the presence of a CO₂ buffer, the catalysts 4Pd-1Cu/SBA-15 and 1Pt-1Cu/SBA-15 reduced at 100°C under H₂ and 1Pd-1Cu/SBA-15 reduced at 200°C under H₂ demonstrated very high nitrate

conversion. Furthermore, the forementioned Pd catalysts had higher N₂ selectivity (88% - 87%) compared to Pt catalyst (80%). Nitrate conversion by the 4Pd-1Cu/SBA-15 catalyst was significantly decreased to 81% in the absence of CO₂.

Keywords

Bimetallic Catalyst, Heterogeneous Catalyst, Nitrate Reduction, SBA-15, XRD, BET, SEM, FTIR, ICP

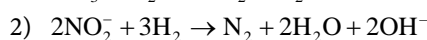
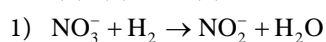
1. Introduction

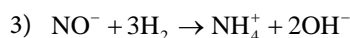
Water quality has been and will continue to be a key global-scale environmental issue, threatening human health, limiting food production, and hindering economic growth [1] [2]. This issue will become more pressing as the world's population continues to grow, the effects of climate change intensify, and the pollution of freshwater resources worsens [3]. Recently, nitrate has emerged as one of the most widespread pollutants in freshwater in many countries [4]. The sources of nitrate contamination originate mainly from the excessive use of fertilizers and uncontrolled land discharges of treated wastewater [5]. Nitrate is highly soluble and stable in water and exposure to elevated levels (>50 mg/L NO₃⁻ in the EU) causes methemoglobinemia in newborns and alimentary canal cancer; no other group of carcinogens produces such a broad type of tumors [6] [7] [8].

Removing nitrate from drinking water is carried out mainly by biological, and physicochemical such as electrodialysis (ED) [9], reverse osmosis (RO) [10] or ion exchange (IE) [11], and electro-reduction technologies [6]. The use of biological denitrification [12], which reduces the nitrates to nitrogen using microorganisms in a biological reactor, is generally preferred to physicochemical methods as it completely removes nitrate by converting it into nitrogen gas; however bacterial contamination and sludge formed limits the wide application of this method [13]. While physicochemical technologies offer high removal efficiency of nitrates, they suffer from low nitrate selectivity. Therefore, the concentrated brine produced by these methods must be post-treated at a high cost. Electro-reduction is another technique to convert nitrates into nitrogen, but nitrite and ammonia are two possible undesired byproducts. So, to make up for the deficiency of the treatment methods developed in the past, nitrate reduction technology using catalysts has appeared [14].

Compared with other methods, the catalyst treatment method showed a higher nitrate reduction rate under relatively different reaction conditions and was evaluated as a cost-effective treatment method [15].

Nitrate reduction reaction using a catalyst is presented as the following formulas (1), (2), and (3).





After nitrate is reduced to nitrite as an intermediate, it is eventually converted into ammonium and nitrogen.

Conversion of nitrates and selectivity towards nitrogen depends mainly on the metal loadings, pH, and catalyst support identity and structure. Several metal loadings and ratios of noble metals (Pd, Pt, Ir, Rh, Ru) and promoter metals (Cu, Sn, In, Ag, Au, Ni) have been used to optimize nitrate reduction into nitrogen gas selectively. However, Pd and Pt as noble metals and Cu and Sn as promoter metals were mainly used with different supports [6].

Recently, several studies highlighted the relevance of the structure and geometry of the support to the catalyst performance reported that supports with high surface area brought about high catalytic activity for nitrate reduction [16] [17]. Also, the noble/promoter metals ratio can differ according to the support used and thus affect both the activity and selectivity of the catalyst [18]. Yoshinaga *et al.* showed that the stability of the metals on the surface of the support at different pH levels depends on the support type [19]. Certain supports have been extensively used in the literature, such as alumina, as it provides a high surface area and stability of metallic particles, while silica offers high selectivity towards nitrogen [20] [21] [22] [23]. Also, carbon-based supports show special surface properties that promote high metal loading and control of porosity [24]. Other supports such as resin [16], Niobium oxide (Nb_2O_5) [25], titanium oxide (TiO_2) [26], calcined alumina [27], silica [28], titania-ceria [26], hydrotalcite [27], and zeolites [28] were explored as well. However, few studies [21] were published on medium-sized porous silica supports, which have advantages in terms of smooth mass transfer of reactants and products, large surface area, chemical resistance, and high chemical and thermal stability. Therefore, more research into medium-sized porous silica supports is required to improve their catalyst performance.

The present study aims to investigate the efficiency of SBA-15 as a support for bimetallic catalysts to reduce nitrate. SBA-15 catalysts were prepared with different noble and promoter metals at different conditions. The prepared bimetallic-SBA-15 catalysts were characterized using several techniques. The performance of bimetallic-SBA-15 catalysts was examined for the conversion of nitrate in water and nitrogen selectivity.

2. Experimental

2.1. Materials

Palladium chloride (99%), copper nitrate (99%), platinum (II) chloride (99%), tin (II) chloride (99%), sodium nitrate ($\geq 99\%$), and sodium borohydride ($\geq 96\%$), obtained from Sigma-Aldrich, were used in the preparation of the bimetallic supported catalysts. Acetone (99.5%), obtained from Scharlau was used for the washing. While chloroform (99.0% - 99.4%), potassiumsodiumtartrate tetrahydrate (99%), sodiumsalicylate (99.5%), sulfuric acid (98%), purchased from

Sigma-Aldrich, and sodium hydroxide (99%), purchased from Riedel-deHaën, were used in the nitratecoloration for the analysis by UV-Vis spectroscopy, hydroxide pellets originated from UNI-CHEM, ammonium chloride, sodium nitroprusside and phenol purchased from Sigma-Aldrich for the ammonia coloration.

2.2. SBA-15 Synthesis

In an open container, 500 ml of ultrapure water is acidified with 79.36 ml of HCl (37%). Then 16.69 grams of the precursor “P123” which is a tri-block polymer (PEOPPO-PEO) was dissolved in the acidic solution. The thermostat attached to the reactor was set at 35°C and the solution was kept under mechanical stirring until a clear solution was obtained. Then 39 ml of “TEOS” silica source was added slowly to the solution using a graduated burette.

Immediately after the addition of TEOS, stirring was stopped and the temperature was maintained at 35°C for 24 hours. After that, the solution was transferred to a sealed polypropylene container, hydrothermally treated at 130°C for 33 hours, and then cooled to room temperature. The solid material was recovered by Buchner filtration, washed 3 times with ultrapure water, and dried 24 hours at room temperature, then recovered and stored. The resulting white powder was then calcined at 500°C in an oven at a heating rate of 2°C/min for 6 hours [29].

2.3. Catalyst Preparation

The bimetallic catalysts with different loadings (1% Pd - 1% Cu, 4% Pd - 1% Cu, 2% Pd - 0.6% Cu, 1% Pd - 1% Sn or 1% Pt - 1% Cu), were prepared according to Li *et al.* method [30]. Typically, the solution of the appropriate metal precursors [PdCl₂; Cu(NO₃)₂, PtCl₂; Cu(NO₃)₂ or PdCl₂; SnCl₂] is prepared with the required amount. Then, the pH value of the solution was adjusted to a value between 11 and 12 by the addition of ammonium hydroxide. Thereafter, 0.2 g of the synthesized SBA-15 was slowly added to the precursor solution, and the mixture was sonicated until it became homogeneous. After stirring for an additional 24 hours, the resulting solid was carefully isolated by filtration, washed with ultrapure water and acetone, dried undervacuum at 65°C for 12 h, the resultant catalyst was reduced with either one of the following two methods:

Method 1: Excess 0.12 g of NaBH₄ dissolved in 20 ml ultrapure water, was added dropwise to the heterogeneous solution (x mg Pd or Pt + y mg Cu or Sn + 200 mg SBA-15 + 250 ml ultrapure water). After sonication at 65°C for 1 h, the mixture was filtered and washed several times with ultrapure water to remove the unreacted reducing agent. Finally, the filtrate was dried under vacuum at room temperature for 5 days.

Method 2: Reduction of the catalyst at 100°C or 200°C for 3 h under an H₂ gas flow after being calcinated for 1 h under an N₂ gas flow [31] [32]. **Table 1** summarizes the prepared catalysts based on their reduction method with its used temperature.

Table 1. The prepared catalysts and their preparation conditions.

Catalyst	Reduction method	Reduction temperature
4Pd-1Cu/SBA-15	NaBH ₄	-----
4Pd-1Cu/SBA-15	H ₂	100 °C
1Pd-1Cu/SBA-15	H ₂	100 °C
1Pd-1Cu/SBA-15	H ₂	200 °C
1Pt-1Cu/SBA-15	H ₂	100 °C
1Pd-1Sn/SBA-15	H ₂	100 °C
2Pd-0.6Cu/SBA-15	H ₂	100 °C

2.4. Catalyst Characterization

The XRD diffractometer small angle (SAXS) was adjusted to identify pores distribution at the surface of SBA-15 used as support for metals. XRD patterns were recorded using a Bruker D8 Advance diffractometer operating in reflection mode at wavelength ($\lambda = 0.154056$ nm) Cu K α (35 Kv, 30 mA) radiation in the 2θ range from 0.8° to 5° in 0.02° steps and a count time of 2 seconds/step. Surface area and isotherms of the supports with or without metals were measured by N₂ adsorption at -196 °C, on a Micromeritics ASAP 2420 analyzer using the multipoint BET method. The morphology and particle size of the supports used were characterized by FEG-TSEM electron microscopy using a JEOL JSM7100F instrument. The Jasco FT/IR-6300 was used to analyze chemical bonds and functional groups of SBA-15. Metal loading for some catalysts was measured by ICP-OES (ICAP 6300 DUO, Thermo).

2.5. Nitrate Reduction

To evaluate the catalytic activity of the nitrate-nitrogen reduction reaction in water, a glass reactor equipped with a magnetic stirrer and gaseous hydrogen (flow rate: 90 ml/min) and carbon dioxide inlet (flow rate: 30 ml/min), capable of generating a reducing atmosphere at 5.5 buffer pH, at room temperature. In a typical run, 25 mg of catalyst was charged into a reactor with magnetic stirrer, containing 50 mL of NaNO₃ solution (30 mg/L NO₃⁻) in ultrapure water. Some reduction experiments were performed in absence of CO₂ flow. After 0.45 μ m microfiltration, the concentration of the unreduced nitrate [33], and ammonium [34] determination respectively, and analyzed with a U-2900 diode array UV-Vis spectrophotometer, where the nitrite is determined using IC chromatography Hitachi Elite Lachrom, auto sampler 2200.

The selectivities for nitrite, ammonium and nitrogen are calculated as follows:

$$S_{\text{NO}_2^-} = \frac{n_{\text{NO}_2^-}}{n_{\text{NO}_3^-} - n_{\text{NO}_3^-}} \quad (1)$$

$$S_{\text{NH}_4^+} = \frac{n_{\text{NH}_4^+}}{n_{\text{NO}_3^-} - n_{\text{NO}_3^-}} \quad (2)$$

$$S_{N_2} = \frac{n_{N_2}}{n_{NO_3^-} - n_{NO_3^-}} \quad (3)$$

where $n_{NO_3^-}$ is the initial amount of nitrate and $n_{NO_3^-}$, $n_{NO_2^-}$, and $n_{NH_4^+}$ are the amount of each species at the end of the reaction. The measures of nitrogen (n_{N_2}) were determined by a mole balance.

3. Results and Discussion

3.1. Catalyst Characterization

The XRD small angle pattern ($0^\circ - 4^\circ 2\theta$) of the calcined SBA-15 sample is shown in **Figure 1**. The typical XRD pattern of SBA-15 has three characteristic peaks relative to the (100), (110), and (200) planes at 2θ of 0.96° , 1.6° , and 1.9° . These peaks characterize the two-dimensional hexagonal structure of SBA-15, which is consistent with the previously prepared SBA-15 using TEOS as the silica source [35].

Figure 2 shows the FT-IR spectrum of the calcined SBA-15 sample prepared

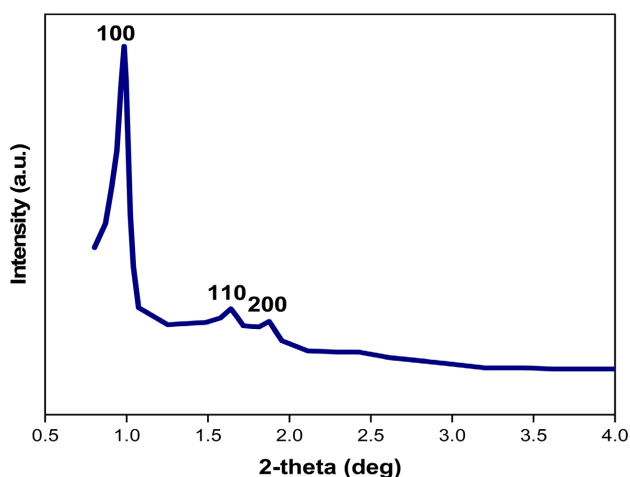


Figure 1. XRD pattern of SBA-15.

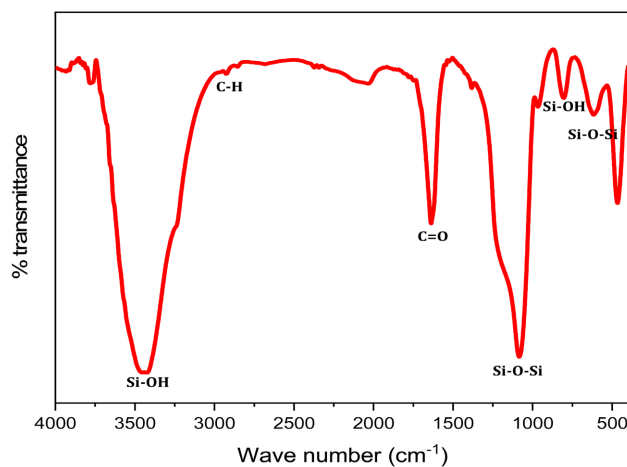


Figure 2. FT-IR spectra of SBA-15.

in this study. The absorption bands of 1082 and 800 cm^{-1} belong to the asymmetric and symmetric extension of the Si-O-Si framework, respectively. The strong band at 3456 cm^{-1} and the weak band at 965 cm^{-1} represent, the stretching and bending vibrations of Si-OH respectively [35] [36]. The presence of small absorption peaks corresponding to the C-H stretching mode (2852 and 2926 cm^{-1}) and bending mode (1384 cm^{-1}) of the tri-block copolymer was also observed [37]. The band at 1636 cm^{-1} is assigned to the stretching vibration of the carbonyl group (C=O) due to the presence of a small amount of surfactant in the sample after calcination.

Table 2 lays out the specific surface area (BET), and average pore size (V_{total}) of the SBA-15 and all of the prepared catalysts. We can notice that the impregnation of metals has not changed the textural characteristics of SBA-15, only slight specific surface area changes are caused by metals impregnation [38]. The specific surface area increases in the case of Sn metal about 4%. The difference between the different values of the specific surface area is due to the role of the various metals used in this study. **Table 2** shows that the temperature does not have any effect on the specific surface area. It seems that SBA-15 imposes its specific surface area and is not very affected by the metal impregnation. In addition, **Figure 3** shows the results of nitrogen adsorption-desorption analysis for

Table 2. BET properties of SBA-15 before and after co-impregnation of metals.

Sample	Reduction temperature	BET surface area (m^2/g)	V_{micro} (cm^3/g)	V_{total} (cm^3/g)
SBA-15	-----	699	0.027	0.985
4Pd-1Cu/SBA-15	100 °C	686	0.022	1.09
1Pd-1Cu/SBA-15	200 °C	684	0.062	1.07
1Pt-1Cu/SBA-15	100 °C	673	0.086	1.03
1Pd-1Sn/SBA-15	100 °C	710	0.016	1.018

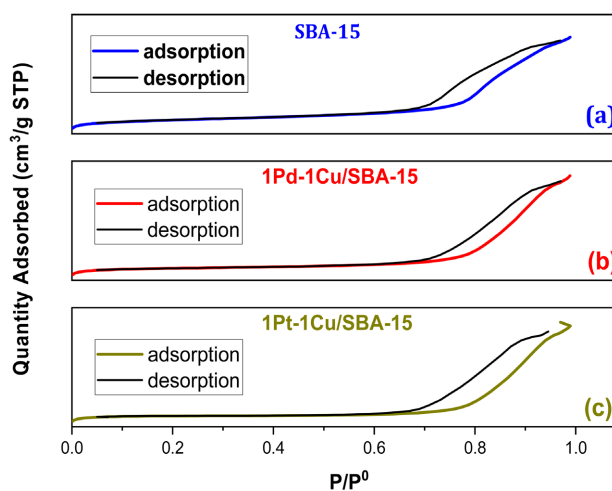


Figure 3. Nitrogen adsorption-desorption isotherm of: (a) SBA-15; (b) 1Pd-1Cu/SBA-15; (c) 1Pt-1Cu/SBA-15.

SBA-15, 1Pd-1Cu/SBA-15 and 1Pt-1Cu/SBA-15. All samples revealed type-IV isotherms with an H1 hysteresis loop at relative pressures (p/p_0) of 0.7 to 1, confirming the presence of cylindrical mesoporous channels [39] and showing uniform pore structure that remains even after metals loading [40].

Table 3 summarizes the measured ICP results of active metal loading for catalysts reduced by NaBH_4 or under H_2 at 100 °C and 200 °C. The results show that 4Pd-1Cu/SBA-15 reduced by NaBH_4 and 1Pd-1Cu/SBA-15 reduced at 100 °C and 200 °C have a measured percentage of both metals close to the nominal values. For 2Pd-0.6Cu/SBA-15 and 1Pd-1Sn/SBA-15, only 1 wt% and 0.87 wt% of Pd are loaded on the support, respectively, while Cu and Sn promoters are not detected (<0.05) in both cases. The difference between nominal percentage and obtained values can be attributed to the interaction between ion metals and the support [41]. According to FTIR results, SBA-15 is highly hydroxylated which results in a high interaction between copper and oxygen surface groups presents on SBA-15, avoiding the close contact of copper with palladium [42] [43] [44]. As a result, active sites could not be completely formed at low reduction temperature (100 °C) on hydroxylated surface [42] so the reduction should be displaced at higher temperatures as observed in the work of Soares *et al.* [45]. It is important to notice that the reduction of copper oxide is promoted by the presence of Pd [45] [46] [47]. Herein we report, the enhancement of active metal loading when 1Pd-1Cu/SBA-15 is reduced at a higher temperature (200 °C).

SEM of SBA-15 and 1Pd-1Cu/SBA-15 are carried out, and the representative photos are shown in **Figure 4**. SEM image of SBA-15 show spherical particles of micrometric size whereas the image of Pd-Cu/SBA-15 shows clearly well dispersed nanosized particles on the surface of SBA-15 that are referred to the supported active metals.

3.2. Catalytic Reduction of Nitrate

3.2.1. Effect of the Reduction Method and the Temperature

Hydrogen gas, commonly used as a reducing agent in bimetallic catalyst preparation, is a highly flammable gas. In an attempt to find an alternative reducing

Table 3. ICP results of the prepared catalysts.

Prepared catalysts	Palladium content (wt %)	Copper content (wt %)	Tin content (wt %)
4% Pd-1% Cu/SBA-15 (NaBH_4)	3.96	0.9	
2% Pd-0.6% Cu/SBA-15 (100 °C)	0.93	<0.05	
1% Pd-1% Sn/SBA-15 (100 °C)	0.87		<0.05
1% Pd-1% Cu/SBA-15 (100 °C)	1.07	0.93	
1% Pd-1% Cu/SBA-15 (200 °C)	0.85	0.89	

agent, NaBH_4 was used. The nitrate conversion percent for the two catalysts (4Pd-1Cu/SBA-15), prepared under H_2 (at 100°C) and NaBH_4 (at 65°C), is shown in **Figure 5**. The catalyst 4Pd-1Cu/SBA-15 reduced by H_2 converted 81% of nitrate, while the catalyst reduced by NaBH_4 converted only 4.3%. This might be due to the fact that SBA-15 has high amount of hydroxyl groups that interact with copper which decreases the reduction power. Thus, thermal reduction under hydrogen is more effective in reducing precursor metals since H_2 reduces CuO at higher temperatures [42]. To further investigate the effect of the reduction temperature on the activity of the supported SBA-15 catalyst, 1Pd-1Cu/SBA-15 was reduced under H_2 at 100°C and 200°C . The results of the nitrate conversion are shown in **Figure 6**. 1Pd-1Cu/SBA-15 reduced at 200°C shows a very high nitrate conversion (96%) compared to 1Pd-1Cu/SBA-15 reduced at 100°C (13%). This result can be explained by the fact that changing the reduction temperature can modify the metal-metal and metal-support interactions that affect the catalytic behavior in nitrate reduction experiments [48]-[52],

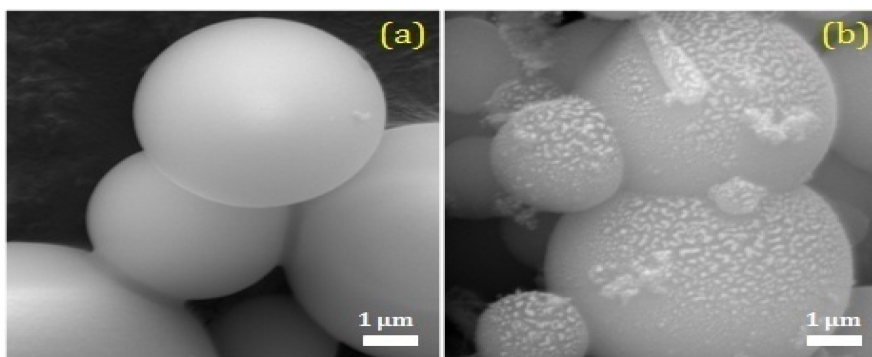


Figure 4. Scanning Electron Microscopy (SEM) images: (a) SBA-15; (b) Pd-Cu/SBA-15.

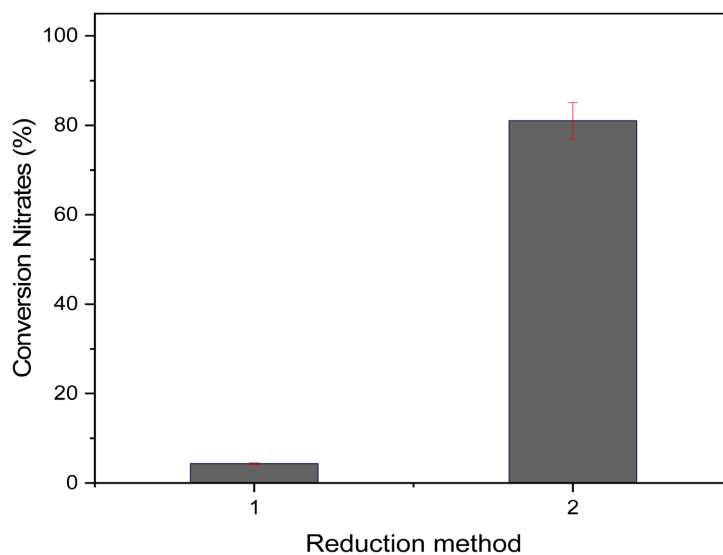


Figure 5. Nitrates conversion (%) analyzed by UV-Vis after 5 h of catalytic reduction using 4Pd-1Cu as a catalyst reduced by two methods. ($C_{\text{NO}_3^-} = 30 \text{ ppm}$, $C_{\text{catalyst}} = 0.5 \text{ g/L}$, Absence of CO_2).

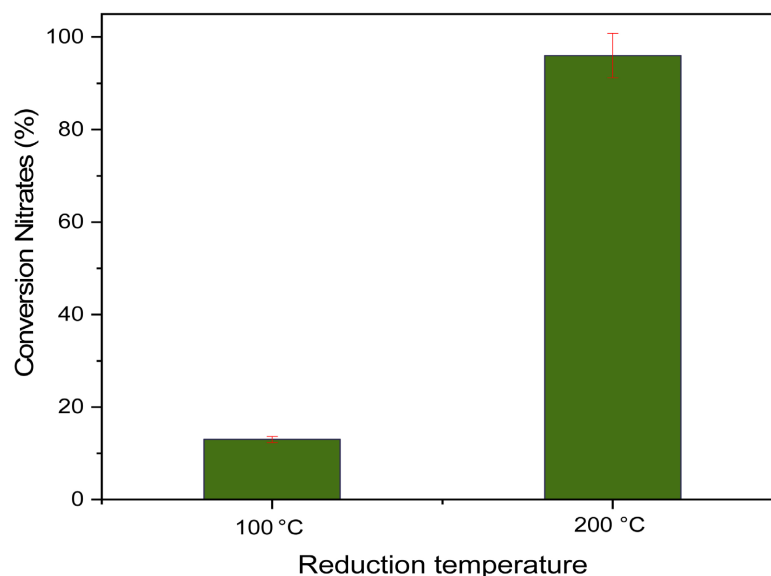


Figure 6. Nitrates conversion (%) analyzed by UV-Vis after 5 h of catalytic reduction using 1Pd-1Cu/SBA-15 as a catalyst reduced with H₂ one time at 100 °C and the other time at 200 °C. ($C_{\text{NO}_3^-} = 30$ ppm, $C_{\text{catalyst}} = 0.5$ g/L, pH = 5.5).

and according to the TPR results already done, it can be noticed that the reduction range of Pd-Cu metals is closer to 200 °C where CuO formation in the presence of an oxygenated surface requires a higher temperature to be reduced, as previously demonstrated for Pd-Cu and Pt-Cu supported catalysts [48].

3.2.2. Effect of CO₂

Figure 7 shows the effect of CO₂ buffering on the catalytic activity of supported catalyst (4Pd-1Cu/SBA-15) reduced under H₂ at 100 °C and investigated after 5 h of reaction, other parameters were kept constant: $C_{\text{NO}_3^-} = 30$ ppm and

$$C_{\text{catalyst}} = 0.5 \text{ g/L} .$$

The catalyst 4Pd-1Cu/SBA-15 showed 100% conversion at pH 5.5 adjusted with CO₂ buffer. In the absence of CO₂, the nitrate conversion significantly decreased to 81% and pH increased from 6.5 to 8 by the end of the reaction.

The basic medium might have a negative effect on the nitrate conversion due the anionic generated groups which repels ion nitrates from the support [48]. As such, we have set the pH to 5.5 by supplying CO₂ for the following catalytic tests.

3.2.3. Effect of the Type of Metal-Supported on Conversion and Selectivity

Nitrate reduction by SBA-15 supported catalysts prepared with different noble/promoter metals and ratios (1Pd-1Cu, 1Pt-1Cu, 1Pd-1Sn, 2Pd-0.6Cu, and 4Pd-1Cu) is shown in **Figure 8**. Catalyst 1Pt-1Cu/SBA-15 exhibited a total conversion of nitrates (100%) after 5 h of reaction while this conversion did not exceed 13% and 6.3% after 5 h for 1Pd-1Cu/SBA-15 and 1Pd-1Sn/SBA-15 catalysts

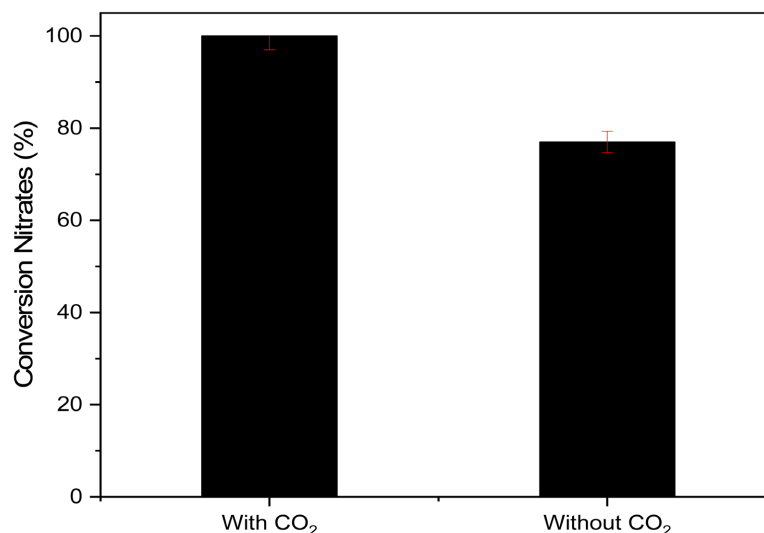


Figure 7. Nitrates conversion (%) analyzed by UV-Vis after 5 h of catalytic reduction using 4Pd-1Cu reduced with H₂ at 100 °C as a catalyst, with CO₂ flow (5.5 pH buffer) and without CO₂ flow. ($C_{\text{NO}_3^-} = 30 \text{ ppm}$, $C_{\text{catalyst}} = 0.5 \text{ g/L}$).

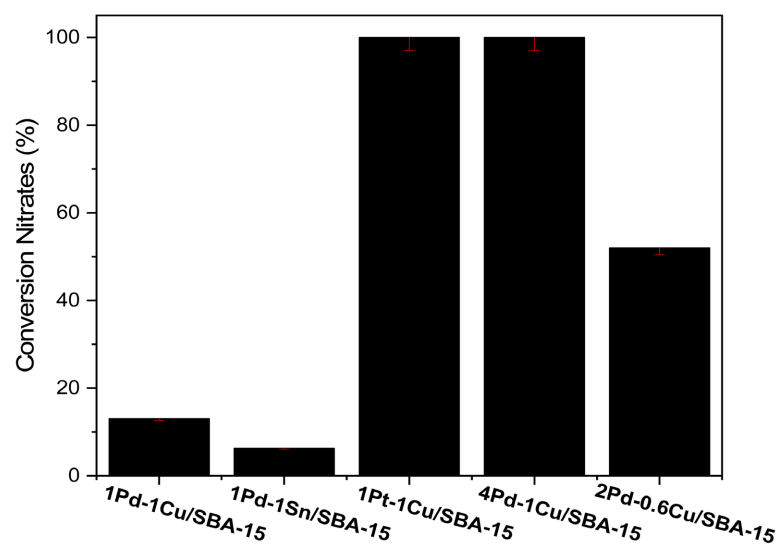


Figure 8. Nitrates conversion (%) analyzed by UV-Vis after 5 h of catalytic reduction using the supported catalysts: 1Pd-1Cu/SBA-15, 1Pd-1Sn/SBA-15, 1Pt-1Cu/SBA-15, 4Pd-1Cu/SBA-15, and 2Pd-0.6Cu/SBA-15 reduced with H₂ at 100 °C. ($C_{\text{NO}_3^-} = 30 \text{ ppm}$, $C_{\text{catalyst}} = 0.5 \text{ g/L}$, pH = 5.5).

respectively. However, as the weight ratio of Pd was increased by a factor of 2 and 4 the conversion was enhanced vastly. Where 4Pd-1Cu/SBA-15 and 2Pd-0.6Cu/SBA-15 showed a 100% and 52% conversion respectively, compared to 13% for 1Pd-1Cu/SBA-15. Thus, the optimum Pd:Cu ratio for efficient nitrate conversion is 4:1. Such a result was also observed by Hörold *et al.* but with other supports [10]. The improved catalytic activity might be caused by the increase in metal loading inside the pores [50]. The selectivity towards nitrate, nitrite, and ammonium is studied for the catalyst that showed almost complete conversion

Table 4. Nitrate conversions ($X_{\text{NO}_3^-}$) and nitrite, ammonium and nitrogen selectivities ($S_{\text{NO}_2^-}$, $S_{\text{NH}_4^+}$, S_{N_2}) of the prepared supported catalysts after 5 h of reaction with CO_2 flow (fixed pH = 5.5).

Catalyst	$t = 300 \text{ min}$			
	$X_{\text{NO}_3^-}$	$S_{\text{NO}_2^-}$	$S_{\text{NH}_4^+}$	S_{N_2}
4Pd-1Cu/SBA-15	1.00	0.00	0.12	0.88
1Pd-1Cu/SBA-15 (200°C)	0.96	0.00	0.13	0.87
1Pt-1Cu/SBA-15	1.00	0.00	0.15	0.80

of nitrate after 5 h of reaction (4Pd-1Cu/SBA-15-100°C, 1Pd-1Cu/SBA-15-200°C, and 1Pt-1Cu/SBA-15-100°C). **Table 4** shows that the selectivity of Pd:Cu bimetallic catalysts towards nitrogen is very high and the selectivity towards ammonium is very low. While the Pt-Cu bimetallic catalyst has lower selectivity towards nitrogen (80%) due to nitrite and ammonium formation, these results are repeated in previous works as in the works of Soares *et al.* [48] [53], and Zhao *et al.* [27] for example where the selectivity towards nitrogen is decreased in the case of Pt-Cu/AC, Pt-Cu/CNT and Pt-Cu/Al comparing it with that in the case of Pd-Cu/AC, Pd-Cu/CNT and Pd-Cu/Al respectively. We can conclude that 4Pd-1Cu-100°C and 1Pd-1Cu-200°C are the optimized catalysts with SBA-15 support for nitrate removal from water in terms of catalytic activity and selectivity to nitrogen at the same time, which is rarely found in previous studied supports.

4. Conclusion

In this study, experiments were carried out on catalysts supported by SBA-15 with changing parameters to show their effect on the catalytic activity. The obtained results showed that SBA-15 is a suitable support catalyst for the nitrate reduction, where a full nitrate conversion is achieved for 4Pd-1Cu/SBA-15 and 1Pt-1Cu/SBA-15 reduced with H_2 at 100°C and 1Pd-1Cu/SBA-15 reduced with H_2 at 200°C. In general, the catalytic activity and the selectivity towards nitrogen or ammonium depend on the method of preparation, the reduction temperature of catalysts, and the experimental conditions of the nitrate reduction. It was observed that the preparation of catalysts with H_2 at high temperatures achieves the formation of active metals and thus improves the efficiency of these supported catalysts in the nitrate conversion. The catalytic activity and the selectivity also depend on the type of metal and the reduction temperature. These parameters affect the metal-support and metal-metal interactions. Nitrogen selectivity is highest for catalysts 4Pd-1Cu/SBA-15 reduced at 100°C and 1Pd-1Cu/SBA-15 reduced at 200°C. SBA-15 is a promising catalyst support for nitrate reduction. This opens new possibilities in the development of novel supported catalysts to improve the catalytic activity and nitrogen selectivity in the remediation of ni-

trate. Further studies on improved nitrate conversion and N₂ selectivity have to be conducted concurrently with tests on catalyst stability. All things considered, testing should be done in natural waters that frequently contain various ions and contaminants that have been shown to provoke deactivation of the catalysts.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Misra, A.K. (2014) Climate Change and Challenges of Water and Food Security. *International Journal of Sustainable Built Environment*, **3**, 153-165. <https://doi.org/10.1016/j.ijbsbe.2014.04.006>
- [2] Tyagi, S., Rawtani, D., Khatri, N. and Tharmavaram, M. (2018) Strategies for Nitrate Removal from Aqueous Environment Using Nanotechnology: A Review. *Journal of Water Process Engineering*, **21**, 84-95. <https://doi.org/10.1016/j.jwpe.2017.12.005>
- [3] Boretti, A. and Rosa, L. (2019) Reassessing the Projections of the World Water Development Report. *NPJ Clean Water*, **2**, 15. <https://doi.org/10.1038/s41545-019-0039-9>
- [4] Martínez, J., Ortiz, A. and Ortiz, I. (2017) State-of-the-Art and Perspectives of the Catalytic and Electrocatalytic Reduction of Aqueous Nitrates. *Applied Catalysis B: Environmental*, **207**, 42-59. <https://doi.org/10.1016/j.apcatb.2017.02.016>
- [5] World Health Organization (2017) Guidelines for Drinking-Water Quality: Fourth Edition Incorporating First Addendum. 4th Edition, World Health Organization, Geneva.
- [6] Fan, A.M. and Steinberg, V.E. (1996) Health Implications of Nitrate and Nitrite in Drinking Water: An Update on Methemoglobinemia Occurrence and Reproductive and Developmental Toxicity. *Regulatory Toxicology and Pharmacology*, **23**, 35-43. <https://doi.org/10.1006/rtph.1996.0006>
- [7] Gray, N.F. (2008) Drinking Water Quality. 2nd Edition, Cambridge University Press, Cambridge.
- [8] Rezvani, F., Sarrafzadeh, M.-H., Ebrahimi, S. and Oh, H.-M. (2019) Nitrate Removal from Drinking Water with a Focus on Biological Methods: A Review. *Environmental Science and Pollution Research*, **26**, 1124-1141. <https://doi.org/10.1007/s11356-017-9185-0>
- [9] Kapoor, A. and Viraraghavan, T. (1997) Nitrate Removal from Drinking Water—Review. *Journal of Environmental Engineering*, **123**, 371-380. [https://doi.org/10.1061/\(ASCE\)0733-9372\(1997\)123:4\(371\)](https://doi.org/10.1061/(ASCE)0733-9372(1997)123:4(371))
- [10] Hörold, S., Vorlop, K.-D., Tacke, T. and Sell, M. (1993) Development of Catalysts for a Selective Nitrate and Nitrite Removal from Drinking Water. *Catalysis Today*, **17**, 21-30. [https://doi.org/10.1016/0920-5861\(93\)80004-K](https://doi.org/10.1016/0920-5861(93)80004-K)
- [11] Huang, C.-P., Wang, H.-W. and Chiu, P.-C. (1998) Nitrate Reduction by Metallic Iron. *Water Research*, **32**, 2257-2264. [https://doi.org/10.1016/S0043-1354\(97\)00464-8](https://doi.org/10.1016/S0043-1354(97)00464-8)
- [12] Mellor, R.B., Ronnenberg, J., Campbell, W.H. and Diekmann, S. (1992) Reduction of Nitrate and Nitrite in Water by Immobilized Enzymes. *Nature*, **355**, 717-719.

- <https://doi.org/10.1038/355717a0>
- [13] Pintar, A. (1999) Catalytic Hydrogenation of Aqueous Nitrate Solutions in Fixed-Bed Reactors. *Catalysis Today*, **53**, 35-50.
[https://doi.org/10.1016/S0920-5861\(99\)00101-7](https://doi.org/10.1016/S0920-5861(99)00101-7)
- [14] Vorlop, K.D. and Tacke, T. (1989) 1st Steps towards Noble-Metal Catalyzed Removal of Nitrate and Nitrite from Drinking-Water. *Chemie Ingenieur Technik*, **61**, 836-837.
- [15] Chen, Y.-X., Zhang, Y. and Chen, G.-H. (2003) Appropriate Conditions or Maximizing Catalytic Reduction Efficiency of Nitrate into Nitrogen Gas in Groundwater. *Water Research*, **37**, 2489-2495. [https://doi.org/10.1016/S0043-1354\(03\)00028-9](https://doi.org/10.1016/S0043-1354(03)00028-9)
- [16] Neyertz, C., Marchesini, F.A., Boix, A., Miró, E. and Querini, C.A. (2010) Catalytic Reduction of Nitrate in Water: Promoted Palladium Catalysts Supported in Resin. *Applied Catalysis A: General*, **372**, 40-47.
<https://doi.org/10.1016/j.apcata.2009.10.001>
- [17] Gao, W., Guan, N., Chen, J., Guan, X., Jin, R., Zeng, H., Liu, Z. and Zhang, F. (2003) Titania Supported Pd-Cu Bimetallic Catalyst for the Reduction of Nitrate in Drinking Water. *Applied Catalysis B: Environmental*, **46**, 341-351.
[https://doi.org/10.1016/S0926-3373\(03\)00226-1](https://doi.org/10.1016/S0926-3373(03)00226-1)
- [18] Santos, A.S.G.G., Restivo, J., Orge, C.A., Pereira, M.F.R. and Soares, O.S.G.P. (2020) Nitrate Catalytic Reduction over Bimetallic Catalysts. *C*, **6**, 78.
<https://doi.org/10.3390/c6040078>
- [19] Yoshinaga, Y., Akita, T., Mikami, I. and Okuhara, T. (2002) Hydrogenation of Nitrate in Water to Nitrogen over Pd-Cu Supported on Active Carbon. *Journal of Catalysis*, **207**, 37-45. <https://doi.org/10.1006/jcat.2002.3529>
- [20] Mendow, G., Marchesini, F.A., Miró, E.E. and Querini, C.A. (2011) Evaluation of Pd-In Supported Catalysts for Water Nitrate Abatement in a Fixed-Bed Continuous Reactor. *Industrial & Engineering Chemistry Research*, **50**, 1911-1920.
<https://doi.org/10.1021/ie102080w>
- [21] Garron, A., Lázár, K. and Epron, F. (2005) Effect of the Support on Tin Distribution in Pd-Sn/Al₂O₃ and Pd-Sn/SiO₂ Catalysts for Application in Water Denitration. *Applied Catalysis B: Environmental*, **59**, 57-69.
<https://doi.org/10.1016/j.apcatb.2005.01.002>
- [22] Marchesini, F.A., Picard, N. and Miró, E.E. (2012) Study of the Interactions of Pd, In with SiO₂ and Al₂O₃ Mixed Supports as Catalysts for the Hydrogenation of Nitrates in Water. *Catalysis Communications*, **21**, 9-13.
<https://doi.org/10.1016/j.catcom.2012.01.015>
- [23] Garron, A. and Epron, F. (2005) Use of Formic Acid as Reducing Agent for Application in Catalytic Reduction of Nitrate in Water. *Water Research*, **39**, 3073-3081.
<https://doi.org/10.1016/j.watres.2005.05.012>
- [24] Trawczyński, J., Gheek, P., Okal, J., Zawadzki, M. and Gomez, M.J.I. (2011) Reduction of Nitrate on Active Carbon Supported Pd-Cu Catalysts. *Applied Catalysis A: General*, **409-410**, 39-47. <https://doi.org/10.1016/j.apcata.2011.09.020>
- [25] Maia, M.P., Rodrigues, M.A. and Passos, F.B. (2007) Nitrate Catalytic Reduction in Water Using Niobia Supported Palladium-Copper Catalysts. *Catalysis Today*, **123**, 171-176. <https://doi.org/10.1016/j.cattod.2007.01.051>
- [26] Constantinou, C.L., Costa, C.N. and Efstathiou, A.M. (2007) The Remarkable Effect of Oxygen on the N₂ Selectivity of Water Catalytic Denitrification by Hydrogen. *Environmental Science & Technology*, **41**, 950-956.
<https://doi.org/10.1021/es061392y>

- [27] Zhao, W., Zhu, X., Wang, Y., Ai, Z. and Zhao, D. (2014) Catalytic Reduction of Aqueous Nitrates by Metal Supported Catalysts on Al Particles. *Chemical Engineering Journal*, **254**, 410-417. <https://doi.org/10.1016/j.cej.2014.05.144>
- [28] Epron, F., Gauthard, F. and Barbier, J. (2002) Catalytic Reduction of Nitrate in Water on a Monometallic Pd/CeO₂ Catalyst. *Journal of Catalysis*, **206**, 363-367. <https://doi.org/10.1006/jcat.2001.3498>
- [29] Vunain, E., Malgas-Enus, R., Jalama, K. and Meijboom, R. (2013) The Effect of Recrystallization Time on Pore Size and Surface Area of Mesoporous SBA-15. *Journal of Sol-Gel Science and Technology*, **68**, 270-277. <https://doi.org/10.1007/s10971-013-3163-x>
- [30] Li, C., Zhang, Q., Wang, Y. and Wan, H. (2008) Preparation, Characterization and Catalytic Activity of Palladium Nanoparticles Encapsulated in SBA-15. *Catalysis Letters*, **120**, 126-136. <https://doi.org/10.1007/s10562-007-9263-x>
- [31] Soares, O.S.G.P., Fan, X., Órfão, J.J.M., Lapkin, A.A. and Pereira, M.F.R. (2012) Kinetic Modeling of Nitrate Reduction Catalyzed by Pd-Cu Supported on Carbon Nanotubes. *Industrial & Engineering Chemistry Research*, **51**, 4854-4860. <https://doi.org/10.1021/ie202957v>
- [32] Soares, O. (2010) Nitrate Removal by Catalytic Reduction with Hydrogen. Faculty of Engineering, University of Porto, Porto.
- [33] Monteiro, M.I.C., Ferreira, F.N., de Oliveira, N.M.M. and Ávila, A.K. (2003) Simplified Version of the Sodium Salicylate Method for Analysis of Nitrate in Drinking Waters. *Analytica Chimica Acta*, **477**, 125-129. [https://doi.org/10.1016/S0003-2670\(02\)01395-8](https://doi.org/10.1016/S0003-2670(02)01395-8)
- [34] Ngo, T.T., Phan, A.P.H., Yam, C.F. and Lenhoff, H.M. (1982) Interference in Determination of Ammonia with the Hypochlorite-Alkaline Phenol Method of Berthelot. *Analytical Chemistry*, **54**, 46-49. <https://doi.org/10.1021/ac00238a015>
- [35] Ivashchenko, N., Gac, W., Tertykh, V., Yanishpolskii, V., Khainakov, S., Dikhtiarrenko, A., Pasieczna-Patkowska, S. and Zawadzki, W. (2012) Preparation, Characterization and Catalytic Activity of Palladium Nanoparticles Embedded in the Mesoporous Silica Matrices. *World Journal of Nano Science and Engineering*, **2**, 117-125. <https://doi.org/10.4236/wjnse.2012.23015>
- [36] Kokunešoski, M., Gulicovski, J., Matović, B., Logar, M., Milonjić, S.K. and Babić, B. (2010) Synthesis and Surface Characterization of Ordered Mesoporous Silica SBA-15. *Materials Chemistry and Physics*, **124**, 1248-1252. <https://doi.org/10.1016/j.matchemphys.2010.08.066>
- [37] Burneau, A., Barres, O., Gallas, J.P. and Lavalley, J.C. (1990) Comparative Study of the Surface Hydroxyl Groups of Fumed and Precipitated Silicas. 2. Characterization by Infrared Spectroscopy of the Interactions with Water. *Langmuir*, **6**, 1364-1372. <https://doi.org/10.1021/la00098a008>
- [38] Min-Sung, K., Lee, M.S. and Lee, K.-Y. (2013) Catalytic Nitrate Reduction in Water over Mesoporous Silica Supported Pd-Cu Catalysts. *Clean Technology*, **19**, 65-72. <https://doi.org/10.7464/ksct.2013.19.1.065>
- [39] Sing, K.S.W. (1985) Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity (Recommendations 1984). *Pure and Applied Chemistry*, **57**, 603-619. <https://doi.org/10.1351/pac198557040603>
- [40] Matei, D., Doicin, B. and Cursaru, D. (2016) Pd/SBA-15 Mesoporous Catalyst for Ethanol Steam Reforming. A Neural Network Approach. *Digest Journal of Nanomaterials and Biostructures*, **11**, 443-451.

- [41] Moriau, L., Bele, M., Vizintin, A., Ruiz-Zepeda, F., Petek, U., Jovanovic, P., Šala, M., Gaberscek, M. and Hodnik, N. (2019) Synthesis and Advanced Electrochemical Characterization of Multifunctional Electrocatalytic Composite for Unitized Regenerative Fuel Cell. *ACS Catalysis*, **9**, 11468-11483. <https://doi.org/10.1021/acscatal.9b03385>
- [42] Soares, O.S.G.P., Órfão, J.J.M., Ruiz-Martínez, J., Silvestre-Albero, J., Sepúlveda-Escribano, A. and Pereira, M.F.R. (2010) Pd-Cu/AC and Pt-Cu/AC Catalysts for Nitrate Reduction with Hydrogen: Influence of Calcination and Reduction Temperatures. *Chemical Engineering Journal*, **165**, 78-88. <https://doi.org/10.1016/j.cej.2010.08.065>
- [43] Biniak, S., Pakuła, M., Szymański, G.S. and Świątkowski, A. (1999) Effect of Activated Carbon Surface Oxygen- and/or Nitrogen-Containing Groups on Adsorption of Copper(II) Ions from Aqueous Solution. *Langmuir*, **15**, 6117-6122.
- [44] Kasaini, H., Goto, M. and Furusaki, S. (1999) Selective Separation of Pd(II), Rh(III), and Ru(III) Ions from a Mixed Chloride Solution Using Activated Carbon Pellets. *Separation Science and Technology*, **35**, 1307-1327.
- [45] Soares, O.S.G.P., Órfão, J.J.M. and Pereira, M.F.R. (2011) Nitrate Reduction in Water Catalysed by Pd-Cu on Different Supports. *Desalination*, **279**, 367-374. <https://doi.org/10.1016/j.desal.2011.06.037>
- [46] Batista, J., Pintar, A., Mandrino, D., Jenko, M. and Martin, V. (2001) XPS and TPR Examinations of γ -Alumina-Supported Pd-Cu Catalysts. *Applied Catalysis A: General*, **206**, 113-124. [https://doi.org/10.1016/S0926-860X\(00\)00589-5](https://doi.org/10.1016/S0926-860X(00)00589-5)
- [47] Mendez, C.M., Olivero, H., Damiani, D.E. and Volpe, M.A. (2008) On the Role of Pd β -Hydride in the Reduction of Nitrate over Pd Based Catalyst. *Applied Catalysis B: Environmental*, **84**, 156-161. <https://doi.org/10.1016/j.apcatb.2008.03.019>
- [48] Soares, O.S.G.P., Órfão, J.J.M. and Pereira, M.F.R. (2010) Pd-Cu and Pt-Cu Catalysts Supported on Carbon Nanotubes for Nitrate Reduction in Water. *Industrial & Engineering Chemistry Research*, **49**, 7183-7192. <https://doi.org/10.1021/ie1001907>
- [49] Sepúlveda-Escribano, A., Coloma, F. and Rodriguez-Reinoso, F. (1998) Platinum Catalysts Supported on Carbon Blacks with Different Surface Chemical Properties. *Applied Catalysis A: General*, **173**, 247-257. [https://doi.org/10.1016/S0926-860X\(98\)00183-5](https://doi.org/10.1016/S0926-860X(98)00183-5)
- [50] Sing, K.S.W. (1982) Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity (Provisional). *Pure and Applied Chemistry*, **54**, 2201-2218. <https://doi.org/10.1351/pac198254112201>
- [51] Parida, K.M. and Rath, D. (2007) Structural Properties and Catalytic Oxidation of Benzene to Phenol over CuO-Impregnated Mesoporous Silica. *Applied Catalysis A: General*, **321**, 101-108. <https://doi.org/10.1016/j.apcata.2007.01.054>
- [52] Roekel, C., Montgomery, D., Singh, J. and Olsen, D. (2022) Analysis of Non-Selective Catalyst Reduction Performance with Dedicated Exhaust Gas Recirculation. *Advances in Chemical Engineering and Science*, **12**, 114-129. <https://doi.org/10.4236/aces.2022.122009>
- [53] Soares, O.S.G.P., Órfão, J.J.M. and Pereira, M.F.R. (2009) Bimetallic Catalysts Supported on Activated Carbon for the Nitrate Reduction in Water: Optimization of Catalysts Composition. *Applied Catalysis B: Environmental*, **91**, 441-448. <https://doi.org/10.1016/j.apcatb.2009.06.013>