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Catalysis Today 123 (2007) 171–176

CATALYSIS TODAY

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Nitrate catalytic reduction in water using niobia supported palladium–copper catalysts

Mônica Pinto Maia, Maíra Andrade Rodrigues, Fabio Barboza Passos [*]

Departamento de Engenharia Química e de Petróleo, Universidade Federal Fluminense,
Rua Passo da Pátria, 156, Niterói, RJ CEP 24210-240, Brazil

Abstract

Niobia and alumina supported palladium catalyst promoted by copper were investigated in the reaction of nitrate catalytic reduction in water and characterized by temperature programmed reduction, physisorption, H_2 chemisorption and X-ray diffraction. Niobia supported Pd–Cu catalysts were as active and selective as an alumina supported catalyst. All catalysts had similar turnover frequencies independent of the support. The control of pH and the interaction between Pd and Cu were critical to improving the selectivity and activity of Pd–Cu/Nb_2O_5 catalysts.
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Keywords: Nitrate removal; Niobia; Hydrogenation

1. Introduction

Water, as a natural resource, has attracted the attention of governments due to its direct relation with economic growth. Water demand has tripled during the last 50 years [1]. Freshwater is a renewable resource in the sense that in the hydrological cycle, water evaporates from oceans and returns partially to land. Salt water represents 97.5% of total water in Earth, but desalinization costs are incompatible with the world economy [2]. Only 2.5% of total water on Earth is present as freshwater, and, most of water is not available for use, because it occurs in the form of glaciers and permanent snow cover (68.8% of total freshwater) ground ice (0.9%) and in groundwater aquifers too deep to access (20.1%). Therefore usable freshwater available in rivers and lakes (0.3%) and shallow groundwater (9.9%) represents only 0.3% of the total water on Earth [3].

The contamination of groundwater by nitrate ion is a concern in several countries [4]. The main sources of contamination are the intense use of fertilizers in agriculture, human sewage and livestock manure. Excessive levels of nitrate in water are detrimental to human health. Besides causing problems with blood pressure, it causes methemoglobinemia in infants [5,6] and studies suggest that nitrate is a precursor of carcinogenic nitrosamines [4,7]. The accepted level of nitrate in water is in the range of 50 mg/L depending on local legislation [8,9].

Considering the need for environment protection, the most interesting option for nitrate removal is its conversion to nitrogen gas [10]. This reaction is catalyzed by modified noble metals, with Pd based catalysts demonstrating the best results to date [11]. Bimetallic Pd–Cu, Pd–Sn, Pd–In and Pd–Zn catalysts exhibit good activity for nitrate reduction [12–15] and high resistance to leaching. The main challenge to this system is maximizing selectivity to nitrogen, and reducing the formation of ammonium ions, whose presence in water is highly undesirable [16].

In this work, niobia supported palladium catalysts promoted by copper were investigated in the nitrate reduction reaction and characterized by temperature programmed reduction, physisorption, H_2 chemisorption and X-ray diffraction. Alumina supported catalysts were previously reported in the literature and were included for comparison.

2. Experimental

2.1. Preparation of catalysts

The γ-Al_2O_3 support was obtained from calcination of a Catapal A (SASOL) bohemite at 550 °C for 2 h in an oven.

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[*] Corresponding author. Tel.: +55 212 629 5599; fax: +55 212 629 5368.
E-mail address: fbpassos@vm.uff.br (F.B. Passos).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.01.051

Several types of niobia were obtained by calcination of hydrated niobic acid (HY340, CBMM) at different temperatures (300, 450, 500 and 550 °C) for 2 h. Pd/Nb_2O_5 and Pd/Al_2O_3 were prepared by incipient wetness technique using $PdCl_2$ (Merck) as a precursor. Bimetallic catalyst was prepared by simultaneous impregnation (incipient wetness) of the supports with $PdCl_2$ and $CuCl_2\cdot 2H_2O$ (Merck). After impregnation, samples were dried at 120 °C for 16 h and calcined at 400 °C for 2 h. The nominal Pd content was 2 wt.% and the Cu nominal content was 0.5 wt.%. The true metal content of the catalysts was measured by X-ray fluorescence.

2.2. *Surface area and pore volume measurements*

Pore volume and surface area measurements were performed in a Micromeritics ASAP 2010 apparatus. About 2 g of each sample was dried in an oven at 120 °C for 16 h, before they were introduced in a quartz cell and attached to the physisorption apparatus. The sample was dried under vacuum at 150 °C for 2 h. The BET surface area, pore volume and mean pore diameter were obtained by N_2 physisorption at −196 °C.

2.3. *Hydrogen chemisorption*

Hydrogen chemisorption was performed by volumetric method in a Micromeritcs ASAP 2010C device. Sample (500 mg) pretreatment consisted of drying at 150 °C for 30 min under a 30 mL/min He flow, followed by reduction under 30 mL/min of H_2 at 25 °C, the same reduction temperature used in the catalytic runs. The samples were outgassed under vacuum of 300 °C before cooling to 35 °C, where all the chemisorption measurements were performed. Both total and reversible H_2 isotherms were measured. H/Pd ratios were calculated using the irreversible H_2 uptake.

2.4. *Temperature programmed reduction*

Temperature programmed reduction (TPR) experiments were performed in a quartz micro-reactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). The samples (500 mg) were dehydrated at 150 °C for 30 min in a He flow prior to reduction. After cooling to room temperature, a mixture of 5% H_2 in Ar flowed through the sample at 30 mL/min, and the temperature was raised at a heating rate of 10 °C/min up to 1000 °C.

2.5. *X-ray diffraction*

X-ray diffraction measurements were made using a Rigaku (Miniflex) diffractometer with a Cu Kα radiation. The XRD data of calcined samples were collected at 0.04°/step with integration times of 1 s/step and a 2θ range of 2–90°.

2.6. *Catalytic tests*

The catalytic tests were performed in a 1 L semi-batch reactor, equipped with a magnetic stirrer and a pH meter. Hydrogen was fed from the reactor bottom increasing the mixing and avoiding diffusion limitations. Initially, 895 mL of deionized water was loaded into the reactor and degassed by flowing H_2 (50 mL/min) for 30 min. After this period, 800 mg of catalyst was added to the reactor and the H_2 flow was kept at 50 mL/min, for 90 min at a stirring rate equal to 500 rpm. The temperature was 25 °C and the reactor was maintained at atmospheric pressure. The reaction started by the addition of 5 mL of a $NaNO_3$ aqueous solution, in order to obtain an initial NO_3^- concentration equal to 100 ppm. Control of pH was performed by flowing CO_2 at 50 mL/min or using a HCl aqueous solution (0.02 M). At these conditions, external diffusion limitations were avoided as demonstrated in preliminary experiments by variation of stirring rates and the absence of internal diffusion resistance was confirmed with the Weisz–Prater criterion.

Small samples of the reactant mixture were periodically taken from the vessel every 10 min. NO_3^- and NO_2^- concentrations were determined by ion chromatography (Dionex ICS 90) using an AS9-HC 4 mm × 200 mm column with a guard column (AG9-HC 4 mm × 50 mm). The mobile phase was a Na_2CO_3 (10 mN) aqueous solution and a H_2SO_4 (50 mN) aqueous solution was used as a regenerator. Ammonium ion concentration was determined by the indophenol method using a spectrophotometer (QUIMIS Q-108D) [17,18]. N_2 yield was calculated as the amount of nitrate converted to N_2 divided by the total amount of nitrate converted.

The reactivity was measured by calculating apparent first order constant rates with respect to nitrate concentration. The effluent gas phase was followed by on-line gas chromatography using a VARIAN 3800 GC equipped with a PORABOND Q capillary column and a thermal conductivity detector.

3. Results and discussion

XRD results confirmed the bohemite and γ-Al_2O_3 structures and N_2 adsorption experiments yielded typical BET surface area and pore volumes for these materials (Table 1). XRD experiments (Fig. 1) demonstrate that upon calcination of niobic acid at different temperatures, different structures are obtained [19]. At calcination temperatures of 300 and 450 °C, samples are amorphous. Increasing the calcination temperature to 500 and 550 °C, there is the formation of T and TT crystalline structures [20]. The surface areas and pore volumes of these

Table 1
BET surface area, pore volume and pore size of supports

Support	Calcination temperature (°C)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Nb_2O_5	550	32.5	0.18	22.8
Nb_2O_5	500	38.6	0.18	14.1
Nb_2O_5	450	107.4	0.18	6.9
Nb_2O_5	300	156.1	0.21	5.5
Nb_2O_5	–	199.9	0.21	4.3
γ-Al_2O_3	550	237.60	0.59	10.0
Bohemite	–	250	0.50	4.5

Table 2
Composition, surface area, pore volume and H_2 chemisorption uptake of Pd–Cu/Al_2O_3 and Pd–Cu/Nb_2O_5 catalysts

Catalyst	Pd (wt.%)	Cu (wt.%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Irrev. H_2[a] (μmol/g_{cat})	H/Pd (%)
Pd/γ-Al_2O_3	2.3	–	242	0.56	9.1	36.0	33.6
Pd Cu/γ-Al_2O_3	2.4	0.86	243	0.55	9.1	32.0	28.2
Pd/Nb_2O_5	2.0	–	89	0.17	7.8	12.8	13.4
Pd Cu/Nb_2O_5	1.90	0.61	83	0.17	8.2	10.9	12.2

[a] Amount of H_2 irreversibly adsorbed at 30 °C.

structures are shown in Table 1. The increase in calcination temperature resulted in a decrease in the BET surface area and pore volume. Several types of supports such as titania, zirconia and tin oxide [21,22] were evaluated in the literature in an attempt to improve the nitrate reduction selectivity. However, one of the observed drawbacks was the difficulty in pH control in the vicinity of the active sites. Due to hydroxyl ion formation during reaction, there is an increase in the local pH value favoring ammonium ion formation. An efficient local pH control should improve the selectivity to nitrogen. Additionally, the pore volume of the support should be considered in order to avoid diffusional effects. All niobia samples investigated in this study showed mesoporosity. Nb_2O_5 calcined at 450 °C was chosen as support for the Pd catalysts, due to its high surface area, stability and mesoporosity. Table 2 displays the metal content of the catalysts measured by X-ray fluorescence and the surface area and pore volume measured by physisorption. The textural properties of the niobia supported catalysts were similar to the pure support. Fig. 2 shows the diffractograms of niobia supported catalysts. Due to the low metal content and indicating relatively, palladium diffraction peaks were not observed. The results indicate there was no modification of the support structure after impregnation of the metal salt.

Temperature-programmed reduction results are displayed in Figs. 3 and 4. For Pd/Al_2O_3 (Fig. 4), PdO reduction at room temperature was observed as reported previously in the literature [23]. Hydrogen consumption around 370 °C, with shoulders at 210 and 280 °C, is due to reduction of PdO_xCl_y surface species [24]. Oxychloride species are formed due to the use of $PdCl_2$ as a precursor. Chloride ions are partially removed from Pd^{2+} with calcination at high temperatures, forming PdO particles [25]. This result indicates the calcination procedure used was not sufficient to remove all chloride ions. The negative peak observed around 70 °C is generally attributed to palladium hydride (β-PdH) decomposition [26]. Adding Cu to the catalyst decreased or even suppressed the intensity of the desorption peak, indicating an inhibition of β-PdH formation [14]. This behavior suggests the formation of Pd–Cu bimetallic species, where the presence of palladium also facilitates copper reduction [14]. The TPR profiles for the Cu/Al_2O_3 catalyst presented two reduction peaks, at 318 and at 512 °C. This behavior is usually attributed to a two-stage reduction of copper

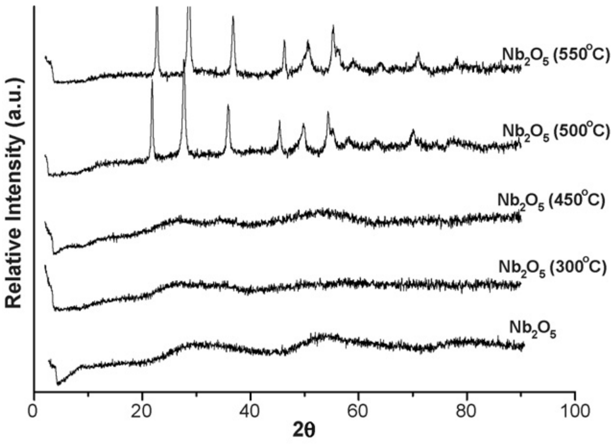

Fig. 1. X-ray diffraction patterns of niobia calcined at different temperatures.

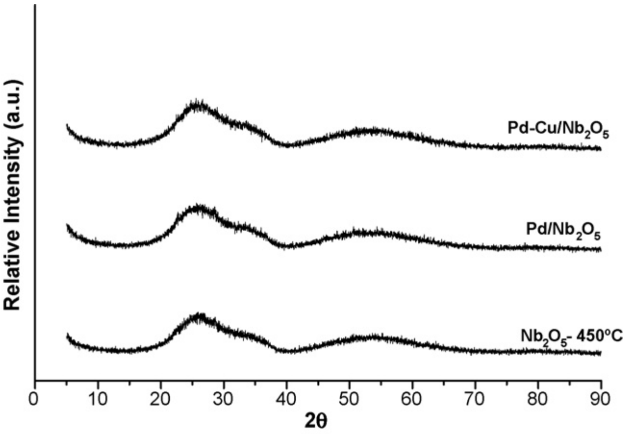

Fig. 2. X-ray diffraction patterns of niobia supported Pd catalysts.

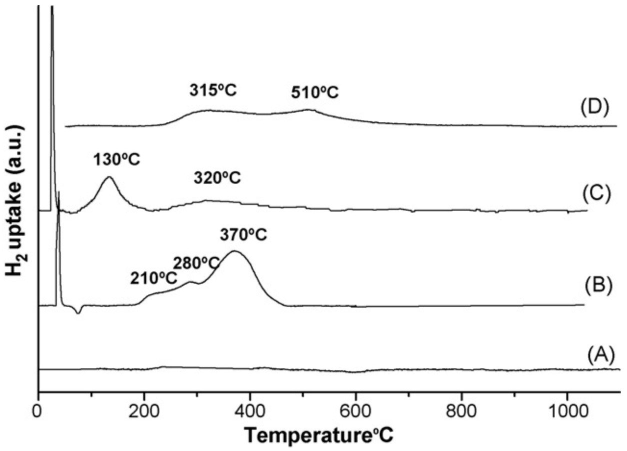

Fig. 3. Temperature programmed reduction profile for γ-Al_2O_3 supported catalysts: (A) γ-Al_2O_3; (B) Pd/γ-Al_2O_3; (C) Pd–Cu/γ-Al_2O_3 (D) Cu/γ-Al_2O_3.

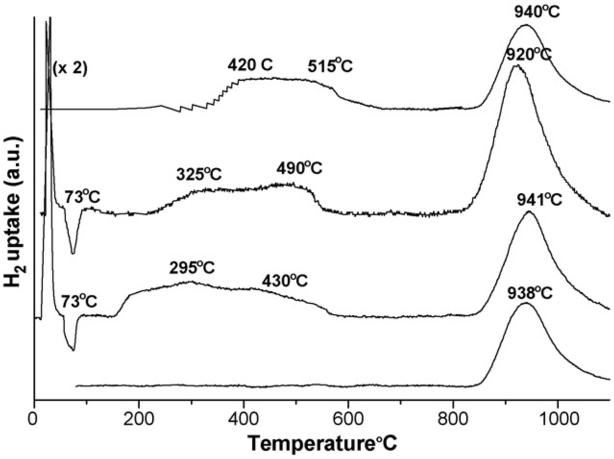

Fig. 4. Temperature programmed reduction profile for niobia supported catalysts: (A) Nb_2O_5; (B) Pd/Nb_2O_5; (C) $Pd–Cu/Nb_2O_5$; (D) Cu/Nb_2O_5.

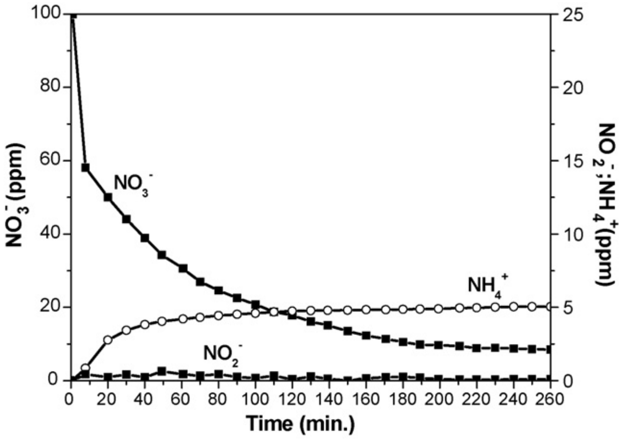

Fig. 5. Nitrate catalytic reduction on $Pd–Cu/Nb_2O_5$ (pH-HCl).

ions [27], the first peak due to the partial reduction of Cu^{2+} ions present in highly dispersed copper oxide species generating Cu^{1+} ions, while the second peak is related to the reduction to Cu^{1+} ions to metallic copper [28–30]. For the 2%Pd–0.5%Cu/γ-Al_2O_3, there is a reduction peak at 133 °C, indicating copper ion reduction at lower temperatures, as compared to Cu/Al_2O_3 catalyst. Sá et al. [31] assigned the copper reduction at lower temperatures to the formation of bimetallic Pd–Cu species and to spillover hydrogen. The small peak observed at 320 °C was previously ascribed to the reduction of highly dispersed copper species [32]. The surface oxychloride species was not observed for the 2%Pd–0.5%Cu/γ-Al_2O_3 profile, because the presence of copper increased the incorporation of oxygen in the coordination of Pd replacing the Cl atoms [24].

Fig. 4 displays the temperature programmed reduction profiles of niobia supported catalysts. The profile for the Nb_2O_5 support displayed a reduction peak only around 940 °C. The profile for Pd/Nb_2O_5 presented a room temperature peak due to PdO reduction, the negative peak due to the decomposition of palladium hydride and a quite broad reduction peak from 150 to 560 °C due to oxychloride surface palladium complex and partial reduction of the support, leading to a strong-metal support interaction (SMSI) state [33]. Cu/Nb_2O_5 profile showed a broad peak around 450 °C, which is only due to CuO reduction as proved by a hydrogen consumption balance [33]. Additionally, the fact that the profile for $Pd–Cu/Nb_2O_5$ was different from the sum of the profiles for the monometallic catalysts indicates an interaction between Pd and Cu [33].

Table 3
Catalytic reduction of nitrate on Pd–Cu catalysts at 25 °C

Catalyst (pH control)	Apparent rate constant (10^{-3} min^{-1})	Initial reaction rate (mmol g_{cat}^{-1} h^{-1})	Conversion (%)[a]	TOF (10^{-2} s^{-1})	NH_4^+ (ppm)[a]	N_2 yield (%)[a]
Pd–Cu/γ-Al_2O_3 (HCl)	33.4	4.0	100	1.8	4.7	84
Pd–Cu/γ-Al_2O_3 (CO_2)	42.1	5.1	100	2.2	3.9	87
$Pd–Cu/Nb_2O_5$ (no control)	3.2	0.39	47	0.49	2.4	30
$Pd–Cu/Nb_2O_5$ (HCl)	11.4	1.4	91	1.8	4.9	91
$Pd–Cu/Nb_2O_5$ (CO_2)	22.6	2.7	100	3.5	3.1	89
$Pd–Cu/Nb_2O_5$ (flow: H_2 80 mL/min and CO_2 20 mL/min)	12.8	1.6	93	2.0	5.0	89
Pd/Nb_2O_5 + Cu/Nb_2O_5 (CO_2)	8.0	0.97	84	1.2	6.0	79

[a] At reaction time equal to 260 min.

Table 4
Activity and selectivity behavior of $Pd–Cu/Al_2O_3$ catalysts in the nitrate reduction

Catalyst	T (°C)	Initial rate (mmol/(h g Pd))	Final NH_4^+ concentration (ppm)	References
5%Pd–1.25%Cu/Al_2O_3	10	60.6	5	[36]
5%Pd–1.25%Cu/Al_2O_3	25	297	4.8	[13]
5%Pd–1.4%Cu	20	294	1	[37]
5%Cu–2%Pd/Al_2O_3	10	313	18	[23]
2%Pd–0.5%Cu/Al_2O_3	25	255	4.7	This work
5%Pd–1%Cu/Al_2O_3	25	139	12	[15]

Fig. 5 shows a typical concentration versus time curve obtained during catalytic reduction of nitrate in our slurry semi-batch reactor with a pH value equal to 5, represented by the results obtained for the 2%Pd–0.5%Cu/Nb_2O_5 (pH controlled with HCl). Upon the reduction of nitrate, there is the formation of nitrogen, rapid formation of ammonium ions and the appearance of nitrite as a reaction intermediate. The analysis of effluent gas phase during reaction showed mainly the formation of N_2 with a very small quantity of N_2O formed. The initial activities calculated assuming apparent first order kinetics are listed in Table 3. The presence of the second metal is necessary to the reaction, as palladium alone is only active for the reduction of the nitrite intermediate [11]. Both Pd/Al_2O_3 and Pt/Nb_2O_5 were not active for the nitrate reduction. Pd–Cu/Al_2O_3 showed an initial rate of reaction equal to 4.0 mmol/(g_{cat} h), which was quite similar to the values reported in the literature [12,22,34,35] as displayed in Table 4.

Pd–Cu/Nb_2O_5 behavior was quite dependent on the pH of the reaction medium (Table 3). When the pH was not controlled, the activity was quite low, with the final conversion attained after 260 min of reaction lower than 50%, and therefore not obeying of the legislation limits of nitrate concentration (50 mg). When the pH was controlled by adding HCl there was an improvement in the catalytic activity, with a 100% conversion being obtained after 260 min of reaction.

Vorlop and Hörold [34] verified that the activity and selectivity of the nitrate reduction strongly depends on the pH value of the reactant medium. Maintaining the medium acidic by pH control, higher values of activity and N_2 selectivity were obtained. During the reaction period, there is as systematic increase in the pH value of the solution originated from hydroxyl ion release to the reaction medium. As the catalyst surface is in dynamic equilibrium with the boundary liquid layer around the catalyst particle, the increase in the pH value in the liquid phase results in the development of a negative charge, which inhibits nitrate adsorption on the surface. Buffering with CO_2 provides a better control of pH inside the pores [10,14], due to a better distribution in the reaction system, avoiding the development of the negative charge on the surface. This effect was observed in our results (Table 3): the use of 50 mL/min of CO_2 flow to control the pH lead to better activity and selectivity. The catalytic tests results also demonstrated it is important to provide enough CO_2 to keep the pH of the solution. When the CO_2 flow rate was decreased to 25 mL/min, the behavior was similar to the case where the pH was maintained by HCl addition (Table 3).

An experiment with a physical mixture of Pt/Nb_2O_5 and Cu/Nb_2O_5 exhibited different performance than the bimetallic catalyst (Pt–Cu/Nb_2O_5). This result indicates the proximity between Pd and Cu is beneficial for the reaction as proposed by Deganello et al. [36,37], but in disagreement with the results observed by Gao et al. [38].

The N_2 yield and the final concentration of NH_4^+ were within the values reported in the literature for Pd–Cu/Al_2O_3 (Table 4). However the final concentrations of NH_4^+ were higher than the recommended level (0.5 ppm).

Turnover rates (Table 3) were calculated using hydrogen adsorption capacity to estimate the number of active sites. Although it is well known that two different sites are necessary for nitrate and H_2 adsorption, this method is standard for the normalization of catalytic reaction rates to the number of surface atoms. The TOF values were of the same magnitude order, indicating structure insensitivity for the catalysts investigated.

4. Conclusions

Niobia supported Pd catalysts were tested in the reduction of nitrate and compared to alumina supported catalysts. The performance of a 2%Pd–0.5%Cu/Nb_2O_5 catalyst was comparable to a 2%Pd–0.5%Cu/γ-Al_2O_3 catalyst for the nitrate reduction in terms of activity and N_2 selectivity. On an active site basis (TOF) Al_2O_3 and Nb_2O_5 supported catalysts presented similar activities, indicating that activity is not related to any change of support on the properties of the active metal. As observed on other supports, the control of pH and the interaction between Pd and Cu were critical for improving the activity and the selectivity of Pd–Cu/Nb_2O_5 catalysts.

Acknowledgements

To CAPES, CNPq and FAPERJ for financial support. To NUCAT/COPPE/UFRJ for the XRD measurements.

References

[1] United Nations Environment Programme, Global Environment Outlook 3, UNEP/Earthscan London, 2002.
[2] P.A. Davis, Desalinization 186 (2005) 97.
[3] I.A. Shiklomanov, World freshwater resources, in: P.H. Gleick (Ed.), Water in Crisis: A Guide to the World's Freshwater Resources, Oxford University Press, New York, 1993.
[4] D.C. Bouchard, M.K. Williams, R.Y. Surampalli, JAWWA 84 (1992) 85.
[5] M.H. Ward, T.M. deKok, P. Levallois, J. Brender, G. Gulis, B.T. Nolan, J. Van Derslice, Environ. Health Perspect. 113 (2005) 1607.
[6] L. Knobeloch, B. Salna, A. Hogan, J. Pstle, H. Anderson, Environ. Health Perspect. 108 (2000) 675.
[7] F.W. Pontius, JAWWA 85 (1993) 12.
[8] C. Revenga, J. Brunner, N. Henninger, K. Kassem, R. Payne, Freshwater Systems, World Resources Institute, Washigton DC, 2000.
[9] A. Scheidleder, J. Grath, G. Winkler, U. Stark, C. Koreimann, C. Gmeiner, Groundwater quality and quantity in Europe, in: S. Nixon (Ed.), European Topic Centre on Inland Waters, European Environment Agency, Copenhagen, 1999.
[10] G. Centi, S. Perathoner, Appl. Catal. B: Environ. 1281 (2002) 1.
[11] A. Pintar, Catal. Today 77 (2003) 451.
[12] L. Leimaignen, C. Tong, V. Begon, R. Burch, D. Chadwick, Catal. Today 75 (2002) 43.
[13] A. Pintar, J. Batista, Appl. Catal. B: Environ. 63 (2006) 150.
[14] M. D'Arino, F. Pinna, G. Strukul, Appl. Catal. B: Environ. 53 (2004) 161.
[15] K.D. Vorlop, T. Tacke, Chem. Ing. Tech. 61 (1989) 836.
[16] C. Molins-Legua, S. Mesenguer-Lloret, Y. Moliner-Martinez, P. Campíns-Falcó, Anal. Chem. 25 (2006) 282.
[17] L.S. Clescerl, A.E. Greenberg, A.D. Eaton (Eds.), Standard Methods for Examination of Water and Wastewater, 20th ed., American Public Health Association, New York, 1999.
[18] Y. Moliner-Martinez, R. Herráez-Hermández, P. Campíns-Falcó, Anal. Chim. Acta 534 (2005) 327.
[19] J.G. Weissman, E.I. Ko, Catal. Today 8 (1990) 27.
[20] I. Nowak, M. Ziolek, Chem. Rev. 99 (1999) 3603.

[21] G. Strukul, R. Gavagnin, F. Pinna, E. Modaferri, S. Perathoner, G. Centi, M. Marella, M. Tomaselli, Catal. Today 55 (2000) 79.

[22] M.J. Chollier-Brym, R. Gavagnin, G. Strukul, M. Marella, M. Tomaselli, P. Ruiz, Catal. Today 75 (2002) 49.

[23] C.E. Gigola, A.M. Sica, Appl. Catal. A: Gen. 239 (2003) 121.

[24] F.B. Noronha, M.A.S. Baldanza, D.A.G. Aranda, A. Ordine, M. Schmal, Appl. Catal. A: Gen. 210 (2001) 275.

[25] F.B. Noronha, D.A.G. Aranda, A. Ordine, M. Schmal, Catal. Today 57 (2000) 275.

[26] G.E. Gdowski, T.E. Felter, R.H. Stulen, Surf. Sci. 181 (1987) 147.

[27] S.J. Gentry, N.W. Hurst, A. Jones, J. Chem. Soc., Faraday Trans. 1 77 (1981) 603.

[28] B.M. Nagaraja, V. Siva Kumar, V. Shashikala, A.H. Padmasri, S. Sreevardhan Reddy, B. David Raju, K.S. Rama Rao, J. Mol. Catal A: Chem. 223 (2004) 339.

[29] F.M.T. Mendes, M. Schmal, Appl. Catal. A: Gen. 151 (1997) 393.

[30] A.J. Rouco, Appl. Catal. A: Gen. 117 (1994) 139.

[31] J. Sá, H. Vinek, Appl. Catal. B: Environ. 26 (2005) 247.

[32] J. Batista, A. Pintar, D. Mandrino, M. Jenko, V. Martin, Appl. Catal. A: Gen. 206 (2001) 113.

[33] F.B. Noronha, R. Frety, M. Primet, M. Schmal, Appl. Catal. 78 (1991) 125.

[34] S. Hörold, K.D. Vorlop, T. Tacke, M. Sell, Catal. Today 17 (1993) 21.

[35] A. Pintar, J. Batista, J. Levec, T. Kajiuchi, Appl. Catal. B: Environ. 11 (1996) 81.

[36] F. Deganello, L.F. Liotta, A. Macaluso, A.M. Venezia, G. Deganello, Appl. Catal. B: Environ. 24 (2000) 265.

[37] A. Pintar, M. Šetinc, J. Levec, J. Catal. 174 (1998) 72.

[38] W. Gao, N. Guan, J. Chen, X. Guan, R. Jin, H. Zeng, Z. Liu, F. Zhang, Appl. Catal. B: Environ. 46 (2003) 341.