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# Characterization of (Sn and Cu)/Pd catalysts for the nitrate reduction in natural water

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ABSTRACT

The aim of this work is to characterize different (Cu and Sn)/Pd catalysts, supported on alumina, used for the catalytic removal of nitrates in natural water. The catalysts have been prepared with a Pd/(Cu or Sn) ratio of 2 but with different metal contents. Their activity and selectivity have been studied using a continuous stirred-tank reactor with nitrate polluted water from an aquifer. The catalysts have been characterized both before and after reaction by XPS, XRD, XRF, adsorption–desorption $N_2$ isotherms at 196 °C and TEM. XPS results show changes of the Pd/Sn surface atomic ratio upon catalyst activation and after reaction and the coexistence of different oxidation states for the active metals. The studied catalysts are active, being the catalyst with the best performance that with the highest metallic dispersion and with the lowest phases segregation. The characterization of the catalysts after reaction shows that catalyst deactivation could be related with the non-reversible oxidation of the Sn–Pd couple.



## 1. Introduction

Nitrates groundwater pollution is an important problem in many rural and populated areas from the world. This pollution is related to the intensive use of fertilizers, the agricultural livestock production industry and by domestic and industrial effluents. In some of these areas, the natural water nitrate concentration is over the permitted limit for the human consumption, which in Europe is 50 mg $L^{-1}$. There are different commercial techniques for removing nitrates from water such as reverse osmosis and electrodialysis. They are effective but they generate a polluted waste that should be treated or disposed of [1]. Another possibility is the use of biological processes which are based on the nitrates reduction to nitrogen using microorganisms [2]. However, there are concerns regarding possible bacterial contamination. Another new technique, still under research is the catalytic reduction of nitrates to nitrogen, using hydrogen as reductant [2–10]. The catalysts used are based in a combination of a noble metal, such as Pd, Pt, Rh or Ir and another metal, such as Cu, Sn, Ag or In [5–8,11–15]. The best results are achieved with Cu–Pd or Sn–Pd catalysts supported on alumina, although recently new catalysts based in Pt have been proposed with very interesting results [16,17]. The problem with this reaction is the formation of undesirable subproducts such as nitrites or ammonia and in order to obtain a commercial catalyst this problem must be solved.

Although some advances have been made in recent years, the role of the different metallic active sites in the catalyst activity and selectivity is not clear. Some studies have appeared recently studying Cu–Pd [4,18–20], Cu–Pt [18] and Pd/$SnO_2$ [21] catalysts by XPS and other techniques. In the case of Pd/$SnO_2$ catalysts, it has been shown [21] that the catalytic activity is governed by the Pd reducibility and the degree of metal-support interaction between Pd and $SnO_2$, where $Pd^{2+}$ is dissolved in the $SnO_2$ support. Although these phenomena can be studied with the aid of spectroscopic X-ray techniques such as photoelectronic spectroscopy (XPS) and fluorescence spectroscopy (XRF), there are not many papers studying other Sn–Pd catalytic systems. This is the case of the Sn–Pd/$Al_2O_3$ catalysts used for the catalytic reduction of nitrates in water. The catalyst characterization by these techniques is required for a better understanding of the catalytic role of the metallic active sites.

On the other hand, the nitrate catalytic reduction has been studied with catalysts used in batch or semi-batch equipment and with distilled water containing nitrates whereas only a few studies have been reported using continuous reactors and with natural water [15,18,22]. In this work we have characterized by different techniques, as XPS, XRD, adsorption–desorption $N_2$ isotherms at −196 °C, XRF and TEM, different Sn–Pd catalysts supported on

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