

# Catalytic reduction of nitrate and nitrite with mono- and bimetallic catalysts supported on pillared clays



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## ABSTRACT

Catalytic reduction of nitrate and nitrite has been carried out under ambient-like conditions (25 °C, 1 atm) with H<sub>2</sub> and CO<sub>2</sub> as reducing and acidifying agents, respectively, using noble metals supported on Al-pillared clays as catalysts. Monometallic catalysts with Ir, Pd, Pt and Rh were tested showing the Pd one the highest activity and the lowest selectivity to ammonium. Bimetallic catalysts with Pd and a second metal (Cu, In and Sn) were prepared and tested for nitrate reduction, all of them yielding higher reaction rates than the monometallic Pd catalyst with very low selectivity to intermediate nitrite. The Pd–In catalyst yielded the lowest selectivity to ammonium (12%). The raw bentonite was acid-treated to prevent the interaction of iron and other cations of the clay structure with the active-phase metals. That treatment improved the activity of the catalysts for nitrate reduction.

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## 1. Introduction

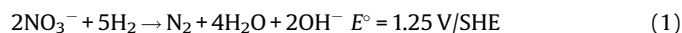
The presence of nutrients, namely nitrate, nitrite, ammonium and phosphate produce undesired effects in water bodies, like algal blooms or eutrophication, which alter the equilibrium of aquatic ecosystems [1,2]. In particular, contamination of groundwater by nitrate is a growing problem due to the intensification of farming and cattle as well as to waste disposal. The World Health Organization (WHO) guidelines give values of 50 and 3 mg/L for nitrate and nitrite, respectively in drinking water.

Different technologies have been developed for the removal of these nitrogen species from water. The most common in the case of municipal wastewater are based on biological nitrification–denitrification. However, biological treatments are not likely for drinking water and searching cost-effective chemical solutions is a challenge in this field. During the last years the potential application of photo-catalytic reduction of nitrate into N<sub>2</sub> with TiO<sub>2</sub> has been studied by several authors [3–7]. Reduction by zerovalent iron has been also investigated [8–10].

A wide diversity of metallic catalysts have been reported so far in the literature dealing with nitrate and nitrite reduction using H<sub>2</sub>

as reducing agent. More than two hundred scientific papers have been published in this field within the last two decades. Pd is by far the most frequently used metal, followed by Pt, although many other metals have been also tested as catalysts and promoters (Cu and Sn are specially representative of these last).

In principle, reduction of NO<sub>3</sub><sup>−</sup> can give rise to the formation of NO<sub>2</sub><sup>−</sup>, NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> in water, and N<sub>2</sub>O and N<sub>2</sub> in gas phase. The Expressions (1) and (2) summarize the process for nitrate reduction:



In that sense a key feature of an effective catalyst is the selectivity towards N<sub>2</sub>, since the other reaction byproducts, especially those in water, are harmful species severely limited by water quality regulations. Yoshinaga et al. [11], working with activated carbon-supported Pd–Cu catalysts, concluded that hydrogen coverage of the precious metal and the morphology of the metal nanoparticles controlled the selectivity to N<sub>2</sub>. Palomares and co-workers [12,13] reported that Pd/hydroxalclites catalysts, whose support presents positive charges and can concentrate anions onto the interlayer space, gave rise to high nitrate conversion into N<sub>2</sub>. These materials were used in an efficient

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nitrate removal system [14]. Denitration of groundwater with Pd–Sn and Pd–Cu based catalysts has been reported by Palomares and co-workers [15,16]. The use of CO<sub>2</sub> has been proposed as a good solution to improve the performance of the catalysts, enhancing the selectivity to N<sub>2</sub> by controlling pH [17].

Regarding the catalyst support, different materials have been used in the literature, being alumina the most widely represented with a growing interest for carbon materials, like activated carbon [18] and carbon nanofibers [19]. Pillared clays (PILCs) have been recently used as catalytic supports for reductive hydrogenation processes, like hydrodechlorination and hydrodenitrogenation of chlorophenols, chlorocresols, chloronitrobenzene or chloroaniline, using precious metals as active phase [20–23]. These materials exhibit thermal and mechanical stability with negligible leaching of the active phase [24]. So far, references on their application in the catalytic reduction of nitrate are scarce [25]. These last authors showed that Pd supported on Al pillared clay is active for nitrate removal.

The aim of this work is to study the reduction of nitrate and nitrite with H<sub>2</sub> using monometallic (Ir, Pd, Pt and Rh) and bimetallic (Pd–Cu, Pd–In and Pd–Sn) catalysts, supported on Al-pillared clays. Besides, the effect of the introduction of CO<sub>2</sub> has been checked for the sake of reducing the selectivity to NH<sub>4</sub><sup>+</sup>. Finally, acid-treated bentonites have been also studied as catalytic support with the purpose of learning on the effect of iron present in the starting clay on the metallic active phase of the catalyst.

## 2. Materials and methods

### 2.1. Preparation of the catalysts

The starting material used to prepare the pillared clays was a purified-grade bentonite supplied by Fisher Scientific Company (Loughborough, OR, USA). The chemical analysis (wt%) of this bentonite was: SiO<sub>2</sub> (52.22), Al<sub>2</sub>O<sub>3</sub> (16.81), Fe<sub>2</sub>O<sub>3</sub>, (3.84), Na<sub>2</sub>O (1.26), MgO (0.88), CaO (0.74), K<sub>2</sub>O (0.80). The Al-pillared clay was obtained following the method described elsewhere [26]. Summarizing, an aluminum pillaring solution was prepared (OH/Al molar ratio=2) and added to a bentonite suspension (1 wt%) providing 10 mmol of Al per gram of clay. The resulting material was washed by centrifugation with deionized water, dried overnight at 110 °C and calcined at 350 °C for 2 h.

The metallic active phase (Ir, Pd, Pt or Rh) used in the monometallic catalysts was introduced into the Al-PILC structure by wet impregnation from IrCl<sub>3</sub> dissolved in water, PdCl<sub>2</sub> in HCl 0.1 M, RhCl<sub>3</sub> in HCl 0.2 M or H<sub>2</sub>PtCl<sub>6</sub> aqueous solution (8 wt% of Pt), respectively. The bimetallic catalysts were synthesized also by wet impregnation of Al-PILC with a Pd/Me (Me: Cu, In, Sn) mixture. All the metallic precursors (PdCl<sub>2</sub>, CuCl<sub>2</sub>, InCl<sub>3</sub> and SnCl<sub>4</sub>) were dissolved in HCl 1 M, except SnCl<sub>4</sub> (liquid) which was added directly to the solution of dissolved PdCl<sub>2</sub> with HCl. The wet solid was dried for 2 h at 25 °C, 14 h at 110 °C and calcined in air atmosphere for 2 h at 500 °C, which was reached at 2 °C/min heating rate. The Pd contents tested were 1 and 5 wt%, always with a Pd:Me ratio of 2:1 (w/w). The catalysts were named by the corresponding metals followed by their nominal percent loading, i.e. Pd-5 refers to the monometallic Pd catalyst with 5 wt% Pd while Pd-Cu (5–2.5) corresponds to the bimetallic Pd–Cu catalyst with 5 wt% Pd and 2.5 wt% Cu.

Other bimetallic catalysts were also prepared using as support a pillared clay synthesized from the same starting bentonite but after a treatment with HCl/HNO<sub>3</sub> (30:70 v/v) during 24 h in order to remove the structural iron. Then, the solid was washed with ultrapure water and dried overnight at 80 °C. This material, named “acid bentonite”, was pillared and impregnated with the different metals using the methods previously described. The catalysts

**Table 1**

Experimental conditions of the nitrate and nitrite reduction experiments.

Experimental conditions	
Reaction temperature	25 °C
Operating pressure	Ambient
Catalyst concentration	0.64 g/L
NO <sub>3</sub> <sup>-</sup> /NO <sub>2</sub> <sup>-</sup> initial conc.	1.61 × 10 <sup>-3</sup> mol/L
Reaction volume	100 mL
Catalyst reduction temperature	100 °C
H <sub>2</sub> flow rate	250 N mL/min
H <sub>2</sub> :CO <sub>2</sub> flow rates	125:125 N mL/min

prepared from this material were identified adding “acid” to the corresponding catalyst name.

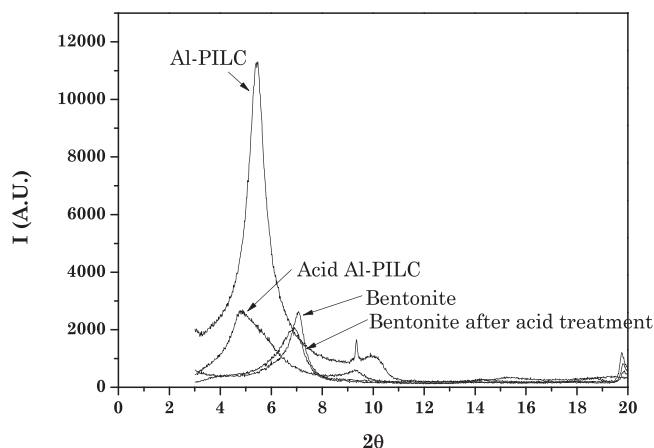
### 2.2. Catalysts characterization

X-ray diffractograms of the bentonite and pillared clays prepared were obtained with a Siemens D5000 diffractometer with CuKα radiation. To maximize the (0 0 1) reflection intensity, oriented clay-aggregate specimens were prepared by drying clay suspensions on glass. The porous structure of the pillared clays and the catalysts was assessed from the 77 K N<sub>2</sub> adsorption–desorption isotherms, obtained in a Micromeritics Tristar 3000 apparatus. The samples were previously outgassed at 160 °C and 5 × 10<sup>-3</sup> Torr for 16 h. The specific surface area was calculated from the BET method (S<sub>BET</sub>). The metal content of the catalysts was measured by X-ray fluorescence with a TXRF EXTRA-II (Rich & Seifert, Germany) spectrometer after digestion of the samples at 100 °C.

The size distribution of the metallic particles was determined by transmission electron microscopy (TEM) using a JEOL 2100F microscope with a point resolution of 0.19 nm. A coupled energy-dispersive X-ray spectrometer (EDXS; INCA x-sight, Oxford Instruments) was used for elemental analysis.

### 2.3. Nitrate and nitrite reduction experiments

The reduction experiments were performed in batch glass reactors (100 mL capacity) at 25 °C and atmospheric pressure using 1.61 mM initial concentration of nitrate and nitrite with 0.64 g/L of catalyst. Internal and external mass transfer limitations were discarded in our working conditions after some preliminary experiments where the effect of bubbling and particle size was checked. The reactor was placed in a thermostatic bath and the experiments were conducted under continuous H<sub>2</sub> or H<sub>2</sub> + CO<sub>2</sub> flow introduced through a fritted glass diffuser.



**Fig. 1.** Diffractograms of the raw material before and after the acid treatment and of the Al-pillared clays obtained from them.

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