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

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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.

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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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