Spectroscopic and catalytic characterization of Pd–In and Pt–In supported on Al$_2$O$_3$ and SiO$_2$, active catalysts for nitrate hydrogenation

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ARTICLE INFO

ABSTRACT

Bimetallic Pt–In and Pd–In catalysts supported on alumina or silica were studied for the reduction of nitrate to N$_2$ in water, using H$_2$ as reducing agent. Characterization results indicate that bimetallic particles with the surface enriched in indium, metallic crystals of Pt or Pd, and oxides of Pt or Pd and In$_2$O$_3$ are the main surface species present in the catalysts.

Several catalysts studied in this work could fulfill the requirements usually established as limit values: 50 ppm of NO_3^-, 0.1 ppm of NO_2^- and 0.5 ppm of NH_4^+. The reaction rate is strongly influenced by either the Pt:In or the Pd:In ratio, the optimum being observed at low contents of In. Of all the catalysts studied in this work, Pd(1 wt.%)In(0.25 wt.%)/Al$_2$O$_3$ is the most active one, but unfortunately, it presents an undesirable high selectivity towards ammonia when nitrate conversion reaches 100%. Pt(1.0%)In(0.25%)/Al$_2$O$_3$ presents a high initial activity but it fastly deactivates during reaction. In general, Pd–In catalysts are more active for nitrate conversion than Pt–In, and alumina is a better support than silica.

The composition of the catalysts changes both after reduction and after contacting the liquid reaction media. These changes have been observed by XPS and TEM. In general, the samples used in the reaction have lower dispersion of metallic phases than the fresh-calcined ones. For most of the catalysts used in this work, the Pt:In or Pd:In surface ratio is lower than the bulk ones, this probably being the reason for the low amount of In that is sufficient to have an optimal performance for nitrate conversion.

1. Introduction

The contamination of water due to both intensive fertilization and waste effluents from industries has produced an increase of nitrate concentration in groundwater. Nitrates are reduced to nitrites in the digestive system, affecting hemoglobin and impairing its function as oxygen-carrier, thus causing the "blue baby syndrome". They are also related to several kinds of cancer, e.g. ovarian and prostate cancers.

At present, the most widespread technologies for the removal of nitrates are biological denitrification and physical chemical processes: ion exchange, reverse osmosis and electro dialysis. However, they present serious problems, e.g. the bacterial process includes handling difficulties, low reaction rates, removal of by-products, low space velocities. Physical–chemical processes only remove the nitrate into brine which has to be treated afterwards or disposed of. Moreover these technologies can be very expensive.

Therefore, increasing attention has lately been paid to a novel technology, still in its development stages: catalytic denitrification [1,2] which employs solid bimetallic catalysts. In this catalytic process, nitrates are reduced to nitrogen using hydrogen; however, undesirable products such as nitrite and ammonium are also formed.

Several solid catalysts have been presented by various authors [3–5]. The catalysts were prepared over different mesoporous supports such as massive oxides, alumina or silica, with the addition of noble metals as Pt or Pd as the main metal, and some second metal such as Cu, Co or In as promoter metal. The possible mechanism for the catalytic reduction is through the combination of active sites in the bimetallic catalyst [6] where the nitrate is reduced to nitrite over the bimetallic particle, and then the nitrite produced is reduced over the noble metal particle to nitrogen or ammonium depending on site selectivity and environmental conditions. Ammonia is a side product which is obtained due to overreduction, and to avoid this a strict control of the reaction media is necessary. Nitrate reduction produces hydroxide ions, and the local accumulation of these could produce a loss of selectivity and activity. The pH can be successfully controlled by adding little volumes of a HCl solution [7].

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In a previous communication [8] we reported that for Pt–In catalysts, bimetallic particles with the surface enriched in indium, probably Pt_2In_3 and/or Pt_3In_7 species, are the active sites for nitrate reduction. In this work, we present a complete study in which Pd–In and Pt–In catalysts are compared with the aim of relating their catalytic activity and selectivity with physicochemical properties. To this end, we used a series of solids with various metal compositions and different supports (SiO_2 and Al_2O_3). XPS, XRD and TEM were chosen as characterization tools, activity and selectivity measurements being carried out in a stirred batch reactor with an on-line pH control.

We have chosen the Pt–In and Pd–In metallic couples because In promoted catalysts have good activity for nitrate conversion and a potential high selectivity to N_2, as reported by other authors [1,6]. Prüsse et al. [6] presented a second generation of nitrate-reducing catalysts which included In as promoter, also describing new concepts such as the use of formic acid as reductant instead of hydrogen. The results obtained in the present work could also be useful to better understand the behavior of bimetallic catalysts in an ionic reaction media, in which bimetallic particles can undergo transformations due to both the reaction itself and the contact with the ionic solution.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by dry impregnation. Aqueous solutions of $PtCl_4H_2$ (10.0 mg mL^{-1}) or $PdCl_2$ (10.0 mg mL^{-1}), and $InCl_3$ (4.6 mg mL^{-1}) were added to 20–40 mesh particles of SiO_2 or Al_2O_3 at room temperature in order to obtain concentrations between 0.5 and 1.5 wt.% of Pt or Pd and between 0.05 and 1.8 wt.% of In. The solids were dried overnight at 393 K and calcined for 2 h, at 773 K in air flow. The supports used were 20–40 mesh Al_2O_3 pellets (Ketjen CK300, surface area: 180 m^2 g^{-1}, pore volume: 0.5 cm^3 g^{-1}) or 20–40 mesh SiO_2 pellets (AESAR Large Pore, surface area: 300 m^2 g^{-1}, pore volume: 1 cm^3 g^{-1})

2.2. Catalyst characterization

2.2.1. X-ray photoelectron analysis (XPS)

The X-ray photoelectron analysis (XPS) was performed with an Axis Ultra DLD (Kratos Tech.) instrument. The samples were mounted on a sample rod placed in the pretreatment chamber of the spectrometer and then evacuated at room temperature. The spectra were excited by the monochromatized Al Kα source (1486.6 eV) run at 15 kV and 10 mA. For the individual peak regions, a pass energy of 20 eV was used. The survey spectrum was measured at 160 eV pass energy. Analyses of the peaks were performed with the software provided by the manufacturer, using a weighted sum of Lorentzian and Gaussian component curves after background subtraction. The binding energies were referenced to the internal C 1s (285.0 eV) standard.

2.2.2. X-ray diffraction analysis (DRX)

X-ray diffractometer patterns were acquired with an XD-D1 Shimadzu instrument, using Cu Kα radiation at 30 kV and 40 mA. The scan rate was 1° min^{-1} in the $2\theta = 10$–$80°$ range.

2.2.3. TEM images

Supported metal particles were observed with a Jeol Electroniç Microscopy, Model 100 CX II operating at 100 kV with 6 Å resolution. The powder was ultrasonically dispersed in ethanol, and the suspension was deposited on a copper grid.

2.3. Nitrate hydrogenation experiments

The reaction test was performed in a three-necked round bottom flask (volume 250 mL) equipped with a magnetic stirrer (700–800 rpm). The pH value was controlled using an automatic pH controller unit. Experiments were carried out at room temperature, pH 5 and atmospheric pressure. Hydrogen was fed by a tube into the solution using a flow rate of 400 mL min^{-1} to ensure the maximum possible hydrogen concentration in solution.

The catalysts were pretreated under a flow of H_2 (100 mL min^{-1}) at 723 K with a heating rate of 10 K min^{-1}. Then, a stirred batch reactor was loaded with 80.0 mL of distilled water, 200 mg of catalyst, and 100 N-ppm of nitrate as initial concentration. Subsequently, a hydrogen flow of 400 mL min^{-1} was fed to the batch reactor. A pH of ca. 5 was maintained during the reaction time by the addition of small amounts of HCl [7].

Small samples were taken from the vessel for the determination of nitrate, nitrite and ammonium using Vis spectroscopy (Cole Parmer 1100 Spectrophotometer) combined with colorimetric reagents. In order to determine nitrates, the Cd Column method and then the colorimetric reaction were used. This colorimetric reaction is the same as the one employed in the assay for nitrites. Ammonium was analyzed by the adapted Berthelot method. The other nitrogen containing compounds were N_2 and small amounts of N_2O in the gas phase, which were not measured.

3. Results and discussion

3.1. Reaction experiments

Fig. 1 shows reaction results for the catalysts studied in this work, containing 1 wt.% of noble metal and different In amounts, from 0.05 wt.% to 1.2 wt.%. In general, it can be seen that Pd–In catalysts reduce nitrates faster that Pt–In ones, and that alumina is a better support than silica, which could be due to the higher PZC value of silica, thus decreasing the rate of adsorption of nitrate ions.

Catalysts containing only noble metals (Pt or Pd), are almost inactive. The addition of a small amount of In (0.05 wt.%) to Pt/Al_2O_3 and Pd/Al_2O_3 increases nitrate conversion and is further increased with 0.25 wt.% of In. However, the addition of higher amounts of In results in lower conversions. A similar behavior is observed in terms of the reaction rate measured at low nitrate conversions; at intermediate In contents an optimum reaction rate is obtained.

In a previous communication [8], for Pt–In catalysts, we reported that the Pt(1.0%)In(0.25%)/Al_2O_3 catalyst shows a very high initial conversion rate but after ca. 15 min, it decreases reaching only 67.7% of conversion at 100 min. The decrease in reaction rate occurred faster than with catalysts with lower Pt:In ratios [8], in such a way, that the initial reaction rate is the highest for the Pt(1.0%) In(0.25%)/Al_2O_3 catalyst, whereas at 60% conversion, it is the lowest. For other catalysts with higher In loadings up to a 1.0:1.2 wt.% Pt:In ratio, both the initial reaction rate and the nitrate conversion decreased as the In loading increased. Note that none of the Pt–In catalysts reached 100% of nitrate conversion after 120 min of reaction. In the case of Pd–In catalysts such deactivation phenomena are not observed, at least in the experiments shown in Fig. 1. In fact, Pd(1.0%)In(0.25%)/Al_2O_3 reaches 100% of nitrate conversion in 40 min.

In addition to nitrogen, certain undesirable products such as nitrites and ammonia were produced. Moreover, even though N_2 is the main gaseous compound formed, nitrogen oxides can also be produced [7]. Daum and Vorlop [9] suggested that nitrogen oxides are reaction intermediates. In Figs. 2 and 3, nitrite and ammonia production against time are shown, respectively. Nitrite is a reaction