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Catalytic hydrogenation of nitrates in water over a bimetallic catalyst

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Abstract

Bimetallic (Pd/Cu) catalysts supported on alumina, which promote the liquid-phase hydrogenation of nitrates, were synthesized using catalytic reduction and consecutive impregnation and were characterized by TEM with EDX, XRD, TPR, BET, and AAS. The catalysts prepared by catalytic reduction have very small particle sizes that are unchanged even after reduction. The two metals are located near each other, as revealed in the EDX profile. Due to the close contact between Pd and Cu, Cu is stabilized in a low oxidation state. The active sites responsible for activity and selectivity in the reduction of nitrates are discussed. These catalysts show high activity for nitrate degradation and good selectivities to nitrogen.

Keywords: Pd-Cu/Al_2O_3; Catalytic reduction synthesis procedure; TEM–EDX; XRD; TPR

1. Introduction

Nitrate concentrations in surface water and especially in ground water, which is the main source of drinking water, are still rising in many parts of the world. The increasing rigorousity of the drinking water quality standards (the legal limits established by the EU are 50, 0.1 and 0.5 ppm for NO_3^-, NO_2^- and NH_4^+, respectively) generates the urgency to develop new technologies for nitrate removal. Several processes have been suggested; the most promising of these appear to be the biologic degradation and catalytic reduction. The approach of these two techniques is the most favourable from the environmental point of view as the nitrates are reduced to nitrogen [1–21].

The catalytic reduction of nitrates is a relatively new approach, which was reported for the first time 15 years ago by Vorlop et al. [1,2] Nitrates are reduced to nitrogen over bimetallic catalysts in the presence of a reducing agent. The catalyst is composed of a noble metal, mainly Pd or Pt and a transition metal such as Cu, Sn, Ag or In, supported on alumina, silica, active carbon, etc. In a later work, Hörold et al. [5] made a screening for highly active catalysts, which reduce nitrate and nitrite mainly to nitrogen. They tested various hydrogenation catalysts, Pd, Pt, Ru, Ir, Rh, Cu and Ni, for their activity and selectivity in the reduction of nitrites to nitrogen. Only the supported Pd catalyst showed a high nitrite removal activity and a low formation of ammonia. The supported Pt catalyst was more active but much less selective than the Pd catalyst under the same experimental conditions. The combination of a noble metal with a group IB metal is often used to improve activity and selectivity for different reactions. A 5% Pd/Al_2O_3 catalyst with different second metals was tested for the reduction of nitrates to nitrogen by Hörold et al. [5]. Within this series the combination of 5% Pd with 1.25% Cu was the most active and selective one. When using iron, cobalt and nickel as second metal only a very small activity and a high selectivity to ammonia was found. Prüsse et al. [22] prepared alumina-supported Pd-Sn and Pd-In catalysts, which were more active for nitrate removal and especially more selective to nitrogen in comparison to alumina-supported Pd-Cu.

Pintar et al. [8] and Wärnå et al. [15] proposed a kinetic model for catalytic nitrate reduction in which the nitrates were reduced via nitrites to nitrogen and ammonia. Nitrites as intermediates and ammonium as by-products are considered the major drawbacks of the process.

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Additionally, the need of a noble metal puts some restrictions on real applications due to its costs. Possible causes for ammonia formation are the rise of the pH during reaction and/or as suggested in the literature [23] isolated Pd atoms, which can act as active sites.

Various preparation techniques are available for the preparation of bimetallic catalysts, for instance, co-precipitation, co-impregnation, incipient wetness impregnation, vapour deposition and catalytic reduction. Epron et al. [14] developed the last procedure, which allows the deposition of a second metal on a pre-reduced parent metal. The authors used Cu as second metal and Pt as pre-reduced parent metal supported on alumina.

The aim of this paper is to show the potential of catalysts synthesized by catalytic reduction [14] in the degradation of nitrates when Pd is used instead of Pt and to compare the activity and selectivity with a 5% Pd, 1.25% Cu supported on alumina catalyst prepared by impregnation.

2. Experimental

2.1. Catalyst preparation

Two types of procedures were applied to prepare the catalysts. The first synthesis procedure, the catalytic reduction, reported by Epron et al. [14], consists of the deposition of copper on the parent noble metal. A 2 wt.% Pd/γ-Al_2O_3 (Pd Com) supplied by Heraeus was used for this preparation.

Five grams of the parent Pd Com catalyst was added to 150 ml of water previously degassed by bubbling nitrogen at room temperature (22–24 °C). The catalyst was then reduced in situ by a counter flow of hydrogen for 2 h. Then, 10 ml of an aqueous solution of $Cu(NO_3)_2$, containing a well-known concentration of salt was added into the suspension containing Pd/Al_2O_3 under a hydrogen flow for 2 h.

Cu ions should be reduced after the following equation adapted for Pd instead of Pt [14]:

$$2Pd{-}H + Cu^{2+} \rightarrow Pd_2Cu + 2H^+$$

It was proved by atomic absorption spectroscopy (AAS) that after the synthesis no copper was present in the solution. The bimetallic catalysts referred to as Pd-Cu CR were then filtered, washed, and dried overnight at 100 °C. After drying, the catalysts were reduced at 350 °C in pure hydrogen for 1 h. This reduction procedure is needed for not only activation of the catalysts but also for the removal of the nitrates adsorbed on the surface. The reduction temperature was chosen based on temperature-programmed reduction measurements in which the nitrates are totally removed as NO at 350 °C.

The second synthesis procedure was an incipient wetness impregnation of γ-Al_2O_3 (Sigma Aldrich ALOX560C, specific surface area of 155 m^2/g, 150 mesh) with aqueous solutions of $Pd(NO_3)_2$ and $Cu(NO_3)_2$ (both from Aldrich) as precursors for the mono- and bimetallic catalysts.

For incipient wetness impregnation the solution volume must correspond to the volume of the pores of the support. This volume was found to be 0.7 ml/g for the used γ-Al_2O_3. The 5 wt.% Pd catalyst was then dried overnight at 100 °C and calcined in air at 450 °C. Afterwards, a second impregnation with $Cu(NO_3)_2$ using the same procedure was carried out. The resulting bimetallic catalyst denoted as Pd-Cu IMP was dried overnight at 100 °C and calcined in air at 450 °C. The catalyst was reduced at 450 °C in pure hydrogen for 1 h. Also Hörold [5] used similar calcination and reduction conditions. The composition of this catalyst was 5 wt.% of Pd and 1.25 wt.% of Cu.

Monometallic catalysts Pd/γ-Al_2O_3 and Cu/γ-Al_2O_3 were synthesized using the procedure described in the last paragraph. The loadings of the metals were 5 wt.% for Pd and 1.25 wt.% for Cu.

2.2. Catalyst characterization

The metal loading was determined by AAS on a Perkin-Elmer 2280 Atomic Absorption Spectrophotometer.

The BET surface areas of the catalysts were obtained in a Quantasorb apparatus. Chemisorption of hydrogen was measured at 80 °C for the palladium monometallic catalyst (Pd Com), in order to determine the number of adsorbed molecules. The catalyst was previously reduced and degassed. Two procedures were applied for the reduction of the catalyst. The first was reduction at 100 °C in pure H_2 for 2 h and the second in water under H_2 at room temperature for 6 h. Degassing of the catalyst was done in N_2 at 400 °C for 2 h. This procedure was applied to remove hydrogen that had been adsorbed during reduction. The measurements were carried out at 80 °C to avoid the formation of Pd β-hydride. According to Mélendrez et al. [24] the presence of Pd β-hydride is avoided when the measurements are done above 70 °C. Also Bastista et al. [25] suggested that Pd β-hydride decomposes at 39 °C.

Temperature-programmed reductions (TPR) were done in a quartz flow reactor. The analyses of the feed and outlet gas streams were performed with a mass spectrometer from Balzers, using a quadrupole as analyser. Samples (75 mg) were activated in helium at 200 °C for 15 min. After activation, the TPR was recorded using a gas feed stream of 10% hydrogen in helium, total flow 18 mL/min, with a programmed temperature ramp of 10 °C/min, which is a standard optimised procedure. Water formation was used as signal for the determination of reduction temperatures because the peaks were better resolved than those of the hydrogen consumption. It should be emphasized that peaks on TPR profiles for water formation were localized in the same position as the ones resulting from hydrogen uptake.

X-Ray diffraction (XRD) patterns were collected using a Philips X'Pert PRO diffractometer (Bragg-Brentano type), with Ni as the internal standard.