



Short Communication

Study of the interactions of Pd,In with SiO₂ and Al₂O₃ mixed supports as catalysts for the hydrogenation of nitrates in water

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ABSTRACT

This paper shows that the combination of Al₂O₃ and SiO₂ as supports of Pd and In allows the modulation of the catalytic properties of nitrate hydrogenation in water in order to improve nitrate conversion and decrease the formation of ammonia. Mechanical mixtures of monometallic catalysts subjected to reduction in hydrogen at 450 °C are efficient catalysts when Pd is supported on Al₂O₃ and In is supported on SiO₂, thus showing considerably high activity and selectivity to gaseous nitrogen compounds when the proportions are 75 wt.% of Pd/Al₂O₃ and 25 wt.% of In/SiO₂. When these monometallic catalysts are reduced separately and then mixed *in situ* in the batch reactor, a moderate activity for nitrate reduction is obtained, suggesting that either some migration of In or Pd occurs in solution generating the bimetallic sites that are necessary to activate nitrate ions, or that a loose contact between In and Pd is enough to initiate the reaction. This contact could be favored by the opposite pzc of both supports.

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1. Introduction

In the last three decades, since the publication of Horold et al. [1], the elimination of nitrates and nitrites by catalytic hydrogenation has been deemed possible. Several catalyst formulations and process configurations have been investigated with the aim of improving the efficiency to reduce nitrates and, at the same time, avoid ammonia formation. Most of the catalysts reported in the literature have been prepared over different supports using Pt or Pd as the main active metal and adding a second metal such as Cu, Sn or In [1–3] as promoter. Monometallic catalysts based on noble metals are inactive for nitrate reduction and the presence of promoters is necessary to initiate the reaction [3–8].

In a recent work, Salomé et al. [9], using several physical mixtures with mono and bimetallic catalysts composed of Rh, Pd, Pt and Cu, were able to demonstrate that the presence of bimetallic sites in the initial catalyst is not mandatory to promote the reduction of nitrate; it is sufficient that the metals become in close contact during the reaction.

On the other hand, in a previous work [10], we reported that Pd, In/Al₂O₃ catalysts are highly active to abate nitrates in water, and that the optimum Pd:In weight ratio is 1:0.25. Similar activity and selectivity results with other catalyst compositions were reported by Prusse et al. [11,12] and Krawczyk et al. [13]. We also observed that SiO₂ supported catalysts, despite their lower activity, are more

selective to N₂ than Al₂O₃ supported ones [15–16]. Thus, the aim of this work is to combine the support properties mentioned above in order to improve catalytic efficiency and to gain further insight into the nature of the metal-support interactions. To this end, we used solids with 1 wt.% Pd and 0.25 wt.% In supported on different mechanical mixtures of SiO₂ and Al₂O₃. Dynamic CO chemisorption, TPR, XRD, and FTIR of adsorbed CO were chosen as characterization tools and the activity measurements were carried out in a stirred batch reactor with an on-line pH control.

2. Experimental

2.1. Catalyst preparation

A series of monometallic (Pd or In) and bimetallic catalysts (Pd,In) were prepared by wet impregnation. Aqueous solutions of Pd (10 mg.mL⁻¹) dissolved in concentrated HCl and/or aqueous solutions of In₂O₃ (4.6 mg.mL⁻¹) dissolved in concentrated HCl were added to SiO₂ (AESAR Large Pore, surface area: 300 m².g⁻¹, pore volume: 1 mL.g⁻¹) or Al₂O₃ (Keene CK300, surface area: 180 m².g⁻¹, pore volume: 0.5 mL.g⁻¹) at room temperature in order to obtain concentrations of 1wt.% Pd and 0.25wt.% In.

Bimetallic catalysts were mechanically mixed in order to obtain different Al₂O₃:SiO₂ weight ratios: 100:0, 75:25, 50:50, 25:75, 0:100. Those catalysts were labeled as 100 m, 75 m, 50 m, 25 m, and 0 m, respectively (see Table 1). Other catalyst series were prepared by co-impregnating both metals over the support mixture with 75:25, 50:50 and 25:75 weight ratios and they were labeled as “c” (see Table 1). Those samples probably had the highest Pd–In contact due

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Table 1
Nomenclature assigned to catalysts.

Catalysts	Label
$Pd,In/Al_2O_3:Pd,In/SiO_2$	
100:0	100 m
75:25	75 m
50:50	50 m
25:75	25 m
0:100	0 m
$Pd,In/(Al_2O_3:SiO_2)$	
75:25	75c
50:50	50c
25:75	25c
$Pd/Al_2O_3:In/Al_2O_3 = 75:25$	AA
$Pd/Al_2O_3:In/SiO_2 = 75:25$	AS
$Pd/SiO_2:In/SiO_2 = 75:25$	SS
$Pd/SiO_2:In/Al_2O_3 = 75:25$	SA

to the way they were prepared. Finally, monometallic Pd/Al_2O_3 , Pd/SiO_2 , In/Al_2O_3 and In/SiO_2 catalysts were mixed in order to obtain mixtures denoted as AS, AA, SA and SS (see Table 1). Those samples presented lower Pd–In contact also because of the way they were prepared.

The solids were dried overnight at 120 °C and calcined at 500 °C in air flow for 2 h. Before the hydrogenation reaction, the catalysts were reduced under H_2 flow at 450 °C for 1 h. In some special cases, monometallic catalysts were reduced at 700 °C.

2.2. Catalyst characterization

Temperature-Programmed Reduction (TPR) experiments were performed on 50 mg of fresh samples in an Okhura TS2002S instrument equipped with a TCD detector using a heating rate of 10 °C/min in a flow of 5% H_2 /Ar (50 mL/min). Dynamic CO chemisorption measurements were carried out by sending 250 μ L pulses of 2.5% CO/N_2 on 0.10 g fresh catalysts, after reduction in H_2 for 1 h at 450 °C. X-ray patterns were acquired with a Shimadzu XC-D1 diffractometer using $CuK\alpha$ radiation and a monochromator with a scan velocity of 1°/min. CO adsorption followed by FTIR analysis was carried out using an IR cell made of glass with CaF_2 windows. The infrared spectrometer was a Shimadzu IR Prestige 21 instrument and the spectra were collected at a resolution of 8 cm^{-1} . The standard wafer pretreatment was a reduction in H_2 at 400 °C for 1 h. Afterwards, the reductant gas was stopped and the system was evacuated at 10^{-6} Torr during 30 min maintaining the temperature at 400 °C. After collecting a reference spectrum for background subtraction at room temperature, the disk was exposed to an 8 Torr of CO. Then, the spectra were collected. This step was repeated at higher CO pressures: 16, 40 and 90 Torr.

2.2.1. Nitrate hydrogenation experiments

A stirred batch reactor was loaded with 80.0 mL of distilled water, 200 mg of catalyst, and 100 N-p $ppmNO_3^-$ as initial concentration. Subsequently, a hydrogen flow of 400 mL/min 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. The catalysts were treated by H_2 bubbling in water before introducing nitrates or nitrites [5]. Experiments performed at different stirring rates between 500 and 1000 rpm showed that the reaction was mass-transfer limited below 600 rpm. Between 600 and 1000 rpm external diffusion limitations were overcome and similar activities were observed. Consequently, 800 rpm was chosen for all experiments.

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

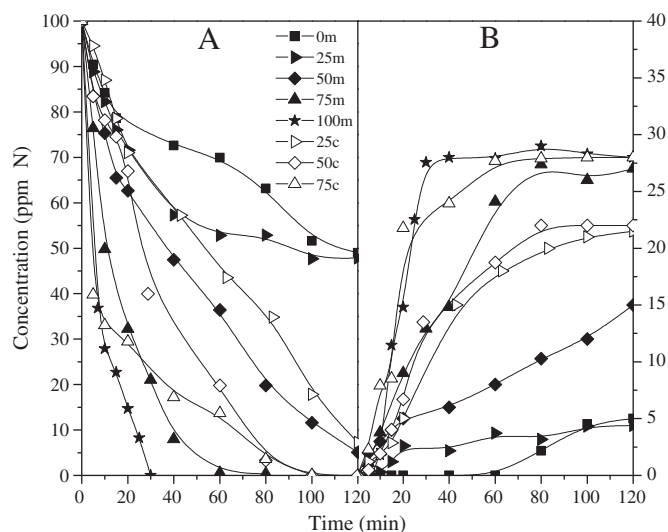


Fig. 1. Nitrates conversion (A), Ammonia production (B). For reaction conditions see Experimental section.

colorimetric reaction were used. This colorimetric reaction is the same reaction employed in the assay for nitrites. Ammonium was analyzed by the adapted Berthelot method.

The initial reaction rate at nitrate conversions lower than 10% was calculated. At low conversions, product concentrations are small; thus, the initial reaction rate (IRR) is an intrinsic property of the active sites towards the nitrate hydrogenation reaction.

3. Results and discussion

3.1. Reaction experiments

Figs. 1 and 2 show nitrate conversion and selectivity results for mixtures of bimetallic catalysts (m) and Pd,In impregnated on mixtures of supports (c). The corresponding values for $Pd,In/Al_2O_3$ (100 m) and $Pd,In/SiO_2$ (0 m) catalysts are also included for comparison. Values of conversions and selectivities measured at 100 min of TOS and the calculated initial rates are summarized in Table 2. As expected, the catalysts with higher alumina content are more active to convert nitrates, and as the proportion of SiO_2 increases, the selectivity to ammonia measured at 50% of conversion decreases, results that are in line with those reported in our previous work [14].

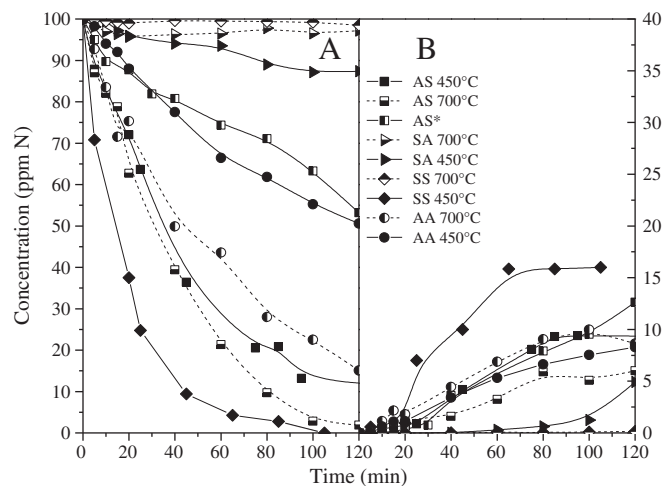


Fig. 2. Nitrates conversion (A), ammonia production (B). For reaction conditions see Experimental section.

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