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Nitrate hydrogenation over Pt,In/Al_2O_3 and Pt,In/SiO_2. Effect of aqueous media and catalyst surface properties upon the catalytic activity

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Abstract

In this work, bimetallic Pt,In catalysts supported on alumina and silica were studied for the reduction of nitrate to N_2 in water, using H_2 as reducing agent. Kinetic and characterization results suggest that the active sites are bimetallic particles with the surface enriched in Indium, probably Pt_2In_3 and/or Pt_3In_7 species. Of all the catalysts studied in this work, Pt(1 wt.%)In(0.25 wt.%)/Al_2O_3 is the most active one. At low time-on-stream it has a very high conversion rate, but it decreases with time due to the segregation of Pt and Indium oxide phases under reacting conditions in the aqueous media. The remarkable high activity of this catalyst during the initial stage of the reaction makes this system very interesting for further studies on the reaction mechanism including the possibility of regenerating the active sites.

Keywords: Nitrates; Nitrites; Catalytic reduction

1. Introduction

Catalytic denitrification is an efficient technology for water purification [1,2] and many solid catalysts have been reported in the literature [3–5]. The possible mechanism for the catalytic reduction is through the combination of active sites in bimetallic catalysts [6] where the nitrate is first reduced to nitrite and then the nitrite is reduced to nitrogen or ammonium depending on the selectivity of the catalyst and the pH of the solution. The aim of this work is to relate the catalytic activity of Pt,In catalysts to their physicochemical properties and analyze how they are affected by the aqueous reaction media.

We have chosen the In,Pt metallic couple because In promoted catalysts have good activity for the nitrates conversion and a potential high selectivity to N_2, as reported by other authors [1–6]. As a matter of fact, 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. On the other hand, in a preliminary screening of different catalysts we found that Pt(1 wt.%),In(0.25 wt.%)/Al_2O_3 has a remarkable initial activity, which decays after some minutes on stream. Therefore, it would also be interesting to get some insight on the origin of this phenomenon.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by dry impregnation. Aqueous solutions of $PtCl_4H_2$ (10.0 mg mL^{-1}) and $InCl_3$ (4.6 mg mL^{-1}) were added to 20–40 mesh Al_2O_3 pellets

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(Ketjen CK300, surface area: 180 m^2/g, pore volume: 0.5 cc/g) or 20–40 mesh SiO_2 pellets (AESAR Large Pore, surface area: 300 m^2/g, pore volume: 1 cc/g) at room temperature in order to obtain 1 wt% of Pt and 0.25, 0.5, 1.0 or 1.2 wt% of In. The solids were dried overnight at 120 °C and calcined for 2 h, at 500 °C .

2.2. Characterization

Temperature Programmed Reduction (TPR) experiments were performed on fresh and used samples in a MICROMERITICS Autochem II measuring the H_2 consumption with a TCD detector (mV signal) after the drying of the gases in a water-trap 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-μl pulses of 2.5% CO/N_2 on 0.10 g samples of fresh and used catalysts, after reduction in H_2 for 1 h at 450 °C.

X-ray diffractometer profiles were acquired with a Shimadzu XC-D1 diffractometer using CuKα radiation and monochromator with a scan velocity of 1°/min.

The X-ray photoelectron analysis (XPS) was performed with an Axis Ultra DLD (Kratos Tech.). The spectra were excited by the monochromatized AlKα source (1486.6 eV) run at 15 kV and 10 mA.

2.3. Reaction experiments

The catalysts were pretreated under a flow of H_2 (100 mL min^{-1}) at 450 °C with a heating rate of 10 °C 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 employed in the assay for nitrites. Ammonium was analyzed by the adapted Berthelot method.

3. Results and discussion

Fig. 1(A) shows that the Pt(1%)/Al_2O_3 catalyst has low activity, and that the nitrate conversion strongly increases after the addition of 0.25wt% In. The In(0.25%)Pt(1%)/Al_2O_3 catalyst shows a very high initial conversion rate but after ca. 15 min, it decreases reaching 67.7% of conversion at 100 min. For the other catalysts with In loading steeply increased up to a 1.0:1.2 wt. Pt:In ratio, the nitrate conversion decreases with the In loading increase (see Fig. 1(A) and Table 1).

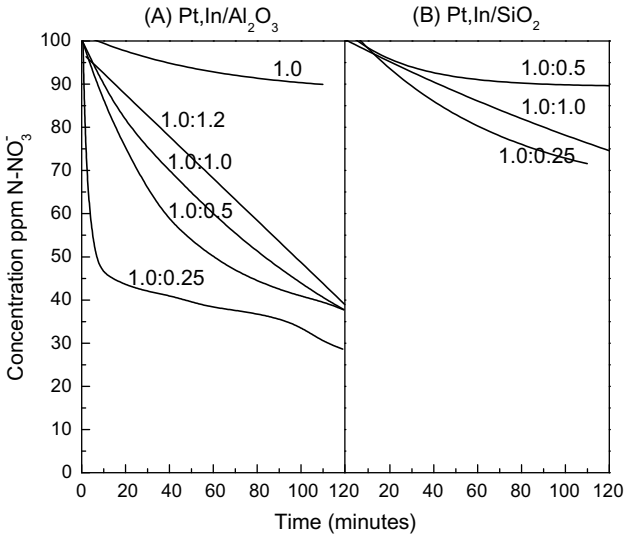

Fig. 1. Nitrate reduction on In promoted Pt catalysts supported on Al_2O_3 (A) and SiO_2 (B). For reaction conditions see Section 2.

Beside nitrogen, undesirable products such as nitrites and ammonia are produced. Moreover, even though N_2 is the main gaseous compound formed, nitrogen oxides can also be produced [8]. Daum and Vorlop [9] suggested that nitrogen oxides are reaction intermediates.

Fig. 2(A) shows that as the reaction progresses, a small increase in nitrites concentration takes place, reaching 2.5 ppm as the maximum value for the catalyst with the highest In content. The other catalysts show lower nitrite production. The most active catalyst for nitrate reduction [Pt(1%)In(0.25%)/Al_2O_3] shows the lowest nitrite formation (0.5 ppm). Results for ammonia production are depicted in Fig. 3(A). In general, higher Pt:In ratios produce higher ammonia concentrations, reaching about 22–23 ppm.

We calculated the initial reaction rates at nitrate conversions lower than 10%. At low conversions, product concentrations are small; thus, the initial rate is an intrinsic property of the active sites towards the nitrate hydrogenation reaction. These results are also shown in Table 1 confirming that the catalyst with the lowest amount of In presents the highest activity and that it steeply decreases when the In content increases. Since the non-promoted Pt(1%)/Al_2O_3 catalyst presents little activity, an optimum Pt:In ratio at about 1%,0.25% is observed. Probably, higher loadings of In hinder the access of H_2 molecules to the Pt crystals.

A series of Pt,In supported on SiO_2 was also prepared in order to gain insight into the effect of the support. Fig. 1(B) shows that the nitrate conversion rates are considerably lower than for Pt,In/Al_2O_3. This fact could be due to the lower PZC value of silica, thus decreasing the rate of adsorption of nitrate ions. The PZC of silica is 3.2, whereas that of alumina is 7.7, and these values do not change significantly with the incorporation of small amounts of Pt and In [10].

Fig. 2(B) shows that for Pt,In/SiO_2, nitrite production occurs to a similar extent if compared with Al_2O_3 sup-