Nitrates Abatment With Pd,In Alumina Supported Catalysts.
Continuous Down Flow Reactor Studies.

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Introduction

The nitrates are proven to be harmful to the human health especially to pregnant women and neonates. The main sources of water contamination with nitrates are from the over use of fertilizers in agriculture, waste effluents from industries and the ground water contamination with septic tanks.

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

The possible mechanism for the catalytic reduction is through the combination of active sites in the bimetallic catalyst 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 [2]. Nitrate reduction produces hydroxide ions, and the local accumulation of these could produce a loss of selectivity and activity [3]. In this study, the stability of P-In catalysts supported on alumina is studied in a flow reactor. Different alternatives for pH control are presented.

Materials and Methods

The catalytic reduction of nitrate was performed in a fixed-bed reactor. The liquid feed solution with 100 mg N-NO₃-/lt was introduced to the reactor by a positive displacement pump. The tubular reactor was filled with 8 g of catalyst. The catalyst (Pd(1%)-In(0.25%)/Al₂O₃) was pretreated under a flow of H₂ at 723 K. Samples were analyzed using Vis spectroscopy combined with colorimetric reagents. Catalysts were characterized by XPS, XRD, CO adsorption-FTIR, TEM, and TPR.

Results and Discussion

Figure 1 shows the results of an experiment in which the volume of water treated was more than 1000 times the volume of catalyst. In Zone A (no pH control), it can be observed a sharp drop in the conversion, possibly due the continuing growth of OH- ions that are generated in the reduction. Also, the concentration of ammonia and nitrites are very high, result that correlates well with results obtained in a batch reactor. In Zone B the pH is adjusted with a solution of HCl. The conversion remains virtually constant, while the selectivity largely improves, as indicated by a major decrease in ammonium and nitrite concentration. In zones C and D the H₂ flow is modified. Increasing the H₂ flow, increases the conversion, but the selectivity to N₂ decreases considerably. In Zone E the pH is adjusted with CO₂ rather than with HCl. This improves significantly the conversion, reaching values close to 60% which are similar to those obtained with fresh catalyst. Besides, the nitrite concentration reduces almost to zero while the ammonium concentration also dropps significantly. Finally the system is fed with a solution of nitrates in alkaline water (Zone F). There was a sharp conversion drop while

the selectivity to nitrite increases. According to these results, in a continous reactor the axial adjustment of pH is critical, as previously suggested [4], and a very good option is to use CO₂ as this will get the best conversion and selectivity. Also, the metal leaching that could occur with HCl is avoided.
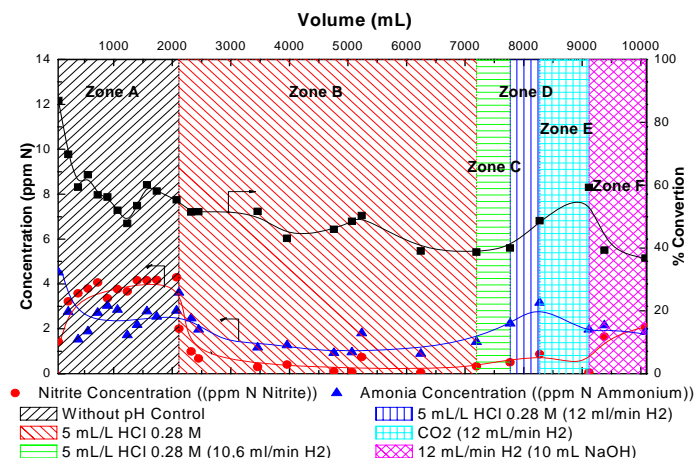

Figure 1. Concentration and convertion profiles as a function of volume.

XPS results indicate that during the reaction there is a modification of the Pd/Al, In/Al and mainly In/Pd. The latter suggests that a surface enrichment in In takes place during the reaction. TPR clearly shows that there is a good interaction between the two metals in the fresh catalyst.

Significance

Bimetallic palladium-based supported catalysts are of great interest in a novel and alternative technology for the removal of nitrate ions from contaminated water in a fixed bed reactor. In this study we have found that the best conditions of operation for high conversion and selectivity are: low flow of hydrogen and controlling the pH with saturated CO₂ feed. The tuning of the In content on these catalysts might lead to an improved selectivity towards the nitrogen production.

References
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