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Microkinetic modeling of the hydrogenation of nitrate in water on Pd–Sn/Al_2O_3 catalyst

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ABSTRACT

An alumina supported palladium–tin catalyst was investigated in the nitrate catalytic hydrogenation in water and was active and selective for the reaction. A reaction mechanism was proposed using a microkinetic model without assuming the rate-determining step of the process. Kinetics measurements were performed in a semi-batch reactor varying the temperature in a range 278–318 K. A statistical fit was achieved with concentration data, obtained from the microkinetic modeling and the experimental practice, providing satisfactory statistical variance.

1. Introduction

The mean concentration of nitrate in underground water has been growing in many parts of the world due to intense industrial and agricultural activity, which is related to an excessive use of chemical fertilizers [1]. High nitrate levels in drinking water is known to be a potential risk to human health and can lead to methaemoglobinaemia in infants (blue-baby syndrome), arterial hypertension, diabetes, thyroid hypertrophy and cancer [2–5]. For this reason, the maximum allowed level of NO_3^- in drinking water is found to be around 50 mg/L depending on local legislation [6].

Among the current remediation available processes, catalytic denitrification is considered the one with the best technical and economical viability and the most environmentally friendly [7]. In this process, nitrate ions react with a reducing agent over a solid catalyst, and are converted mainly to gaseous nitrogen. The main drawback of this process is the production of ammonia as a by-product [8].

The prevailing reaction seems to consist of two stages: in the first one, the nitrate reduction to nitrite takes place (Eq. (1)), and in the second one, which is the selectivity determinant, the formation of N_2 or NH_4^+ takes place, in parallel reaction (Eqs. (2) and (3)) [9–13].

$$NO_3^- + H_2 \rightarrow NO_2^- + H_2O \quad (1)$$

$$2NO_2^- + 3H_2 \rightarrow (NO, N_2O) \rightarrow N_2 + 2H_2O + 2OH^- \quad (2)$$

$$NO_2^- + 3H_2 \rightarrow NH_4^+ + 2OH^- \quad (3)$$

Typical catalyst employed for nitrate reduction are composed of a noble metal, which is responsible for the reduction of nitrite and a non-noble metal, which acts as an activation promoter for the first reaction step. Both metals are supported on a metallic oxide; the most selective noble metal was found to be palladium and the best coadjutant metals were found to be either Cu, Sn and In [14–16]. Palladium catalysts are also active when a reducible support such as TiO_2, SnO_2 or CeO_2 is used [36–38].

There can be found many recent works devoted to the study of nitrate catalytic reduction aiming the improvement of both activity and selectivity with respect to N_2 production [39]. Nevertheless, there is still little information about this reaction kinetics. Some works [17–19] were restricted to the linearization of Arrhenius equations, some others [9,20] established models based on Langmuir–Hinshelwood equations, but the related data were not statistically treated and a no clear analysis of the limiting reaction step was presented and, finally, Salazar et al. [21] employed Langmuir–Hinshelwood–Hougen–Watson model for a adequate statistical data analysis, but considered only the first reaction step.

Fan et al. [34] have proposed a mechanistic model for catalytic reduction of nitrate based on a mixed flow reactor experimental results. The present work was devoted to the study of a microkinetic framework for the nitrate catalytic reduction over a Pd–Sn/Al_2O_3

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