

Perovskites Catalysts for a Green Nitric Acid Production: Kinetics and Modeling

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Introduction

The production of nitric acid, base product of nitrogen chemistry (agro-chemistry, pharmacy, explosives, polymers), involves ammonia oxidation into nitric oxide. This reaction is catalyzed by platinum-rhodium gauzes and takes place at high temperature (~900°C) with a very short contact time (10^{-3} - 10^{-4} s).

The ammonia oxidation reaction produces three products: N_2 , N_2O and NO ; Only NO is desired and selectivities around 95-97% are achieved with the current catalyst, depending on temperatures and pressures. The selectivity to N_2O amounts only to 1.5-2.5%, but it causes environmental problems as it is the major source of NO_x in the stratosphere and it also contributes to the greenhouse effect. Different strategies are possible to reduce N_2O in a nitric acid plant [1]. The most elegant, but also most difficult is to replace the platinum based catalyst with one less selective to N_2O .

Previous studies [2] claim that metal oxides of cobalt, iron or manganese show high selectivity to NO , but suffer from lack of long-term stability. Other studies emphasize that the use of perovskites type ABO_3 [3] give similar results as platinum. Consequently trials to optimize this type of material by formulation or doping are being investigated. Within this goal, a kinetic study has been carried out for a better understanding of the reaction mechanism over oxides.

Materials and Methods

Annular reactor

Due to the severe reaction conditions and the resulting high rate of reaction, intrinsic kinetics are not attainable in a fixed bed reactor configuration. Instead an annular reactor configuration was used in this study, offering the advantages of low pressure drop, a thin catalyst layer and isothermal conditions. Despite this improved reactor concept the data over the most active catalysts still were mass transfer limited when confronted with the criteria given by Berger and Kapteijn [3]. Therefore a reactor model was developed that takes into account mass transfer to the catalyst layer.

Analytical Procedure

Reactants and products concentrations have been analyzed by two online analysis systems.

The first one is a modified IR analyzer (Nicolet 380 FT-IR) consisting of an infrared source, a mirror system and a light-pipe. The second system is a micro GC (Agilent M200) containing two columns, which enabled to follow N_2 , O_2 , N_2O and CF_4 . CF_4 is used as an internal standard.

Catalyst

Three different perovskites $LaMnO_3$, $LaFeO_3$, $LaCoO_3$, have been synthesized by both the citrate and Pechini methods. XRD analysis showed crystalline materials that could be attributed almost entirely to perovskite structures.

Results and Discussion

Numerous reactions between NH_3 , O_2 , NO , NO_2 , N_2O , N_2 and H_2O may occur and the majority of these reactions have very high values of the equilibrium constants at the reaction temperatures. A first step is to establish a proper reaction network that is able to account for all the reaction intermediates and products with a limited amount of reactions. The reaction network presented in Figure 1 has been established by studying the reaction of the products and intermediates as well as by modeling the data by means of power law rate equations. It was found that the gas phase equilibrium between NO and NO_2 has to be taken into account. NO_2 then further reacts with NH_3 to N_2 . Another route to the formation of N_2 is through the formation of N_2O that can be further reduced to N_2 . This reaction network was used for modelling all three perovskites. Having established this reaction network the individual reaction can be described adequately by a Mars-Van Krevelen based rate equation. Figure 2 shows the comparison of the experimental data with the model predictions over $LaCoO_3$.

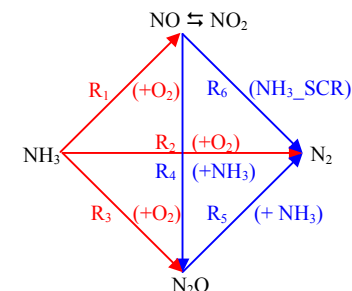


Figure 1. Reaction network considered

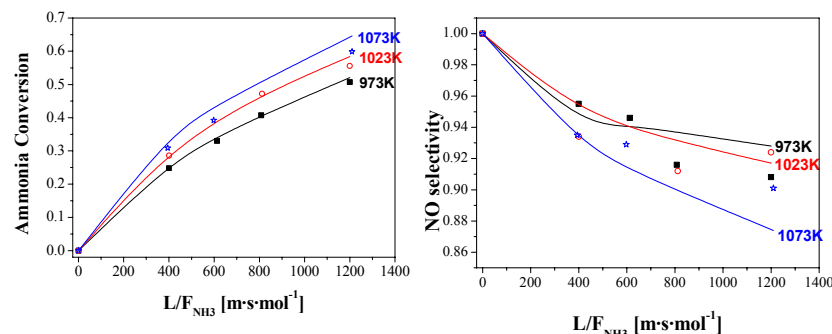


Figure 2. Ammonia conversion (left) and NO selectivity (right) as function of the contact time (L/F_{NH_3}) over $LaCoO_3$

References

- [1] J. Pérez-Ramirez, F. Kapteijn, K. Schöffel, J.A. Moulijn, *Appl. Catal. B: Environ.* 44 (2003) 117–151.
- [2] V. A. Sadykov, L. A. Isupova, I. A. Zolotarskii, L. N. Bobrova, A. S. Noskov, V. N. Parmon, E. A. Brushtein, T. V. Telyatnikova, V. I. Chernyshev and V. V. Lunin, *Appl. Catal. A: General* 2000, 204, 59-87.
- [3] Wu, Y., Yu, T., Fan, Z. R. and Wang, L. C., *J. Catal.* 1989, 120, 88-107.
- [4] R. J. Berger and F. Kapteijn, *Indus. & Eng. Chem. Res.* 2007, 46, 3863-3870.