Analysis of the adsorption rate on catalysts for ammonia synthesis

Simon I. Hansen[1], Anker D. Jensen[1] and Jakob M. Christensen[1]*
[1]*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads 228A, 2800 Kgs. Lyngby (Denmark)*
*jmc@kt.dtu.dk

Introduction

The synthesis of ammonia is an important chemical process as ammonia is an essential component of synthetic fertilizer and an energy carrier in Power-to-X processes. With an annual production of 180 million tons (making it one of the most produced chemicals), the synthesis of ammonia accounts for approximately 2 % of the global energy consumption and constitute 1 % of carbon dioxide emissions globally [1]. Currently, the Haber-Bosch process developed in the beginning of the 20th century is still used to produce ammonia, but despite the maturity of this technology, the process may not be fully understood. However, it is widely accepted that the rate determining step is the breaking of the N≡N triple bond [2-3].

The reaction is believed to occur via a dissociative mechanism where molecular nitrogen is adsorbed onto the catalyst surface and the internal N≡N bond is broken without any interaction with hydrogen [4]. However, studies have shown that an H_2/D_2 isotope effect exists, where D_2 gives a three-four times faster reaction rate than H_2 [5-6]. This is interesting since H_2 is not part of the rate determining step in the dissociative mechanism. A greater understanding of the dissociative N_2 adsorption, its coverage dependence and the nitrogen coverage prevailing during the reaction is necessary in order to clarify these discrepancies in the mechanistic understanding.

Materials and Methods

An iron-based catalyst promoted with K and Al was used to carry out experiments on N_2 adsorption. The catalyst particles (150-300 µm) were placed in a glass-lined packed bed U-tube reactor. The adsorption was carried out in a 100 NmL/min flow at 400 °C, 1 bar with 25% N_2 and varying H_2 content (balance Ar). The adsorption times were varied by applying a quenching method developed in our research group [7]. N_2-TPD with a 2 °C/min ramp was then performed to analyze the surface coverage. The N_2 content of the gas during the TPD was monitored by mass spectroscopy. The adsorption rate was determined from the adsorption time and the resulting surface coverage.

The experimental data was modelled to describe the rate of adsorption. A modified Arrhenius expression as described below was used to model the data:

$$\frac{d\theta}{dt} = A_{ads}\, exp\left(-\frac{E_{ads}}{RT}\right) p_{N_2}(1-\theta)^2 - A_{des}\, exp\left(-\frac{E_{des}}{RT}\right)\theta^2$$

$$E_{ads} = E_0 + q_1\theta^2 \quad \wedge \quad E_{des} = E_{ads} + \Delta H \quad \wedge \quad \Delta H = \Delta H_0 - q_2\theta^2$$

Results and Discussion

The data collected during the TPD experiments was baseline corrected and integrated to determine the fractional surface coverage of N. The results are shown in Figure 1. The results show that as more nitrogen is adsorbed, it is more easily desorbed as the initial desorption occurs at lower temperatures. Moreover, the desorption peak is also at a lower temperature at higher coverage. A second peak at high temperature (around 600 °C) is also observed, which is likely due to intercalated nitrogen.

The model includes a quadratically decreasing heat of adsorption with increasing coverage on the basis of electrostatic arguments, and the validity of this dependence has been verified by comparison with experimental data reported in the literature [8]. The model has also been fitted to experimental data from the TPD in order to obtain an expression describing the ad- and desorption rates of nitrogen. The fitted model is shown in Figure 1. Moreover, this study also includes adsorption with hydrogen in the adsorption gas, which indicate that the adsorption rate is increased when hydrogen is present. However, the observed adsorption rates do not correspond to the measured NH_3 synthesis rate, which accentuate that the process has not been fully understood yet and hence, more research is required.

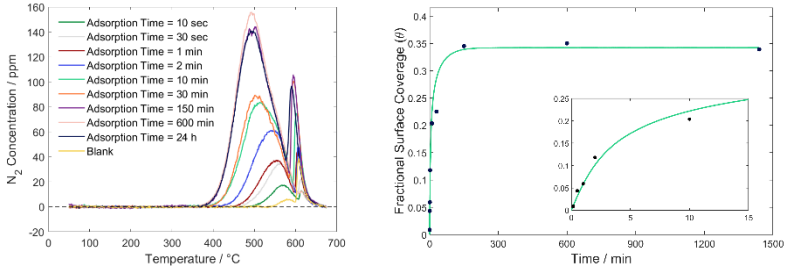

Figure 1. *Left panel:* Baseline corrected data from the TPD experiments performed after adsorption (400 °C, 1 bar, 25 % N_2 (balance Ar)) for various time periods. *Right panel:* Model (green) describing the fractional surface coverage of nitrogen as a function of adsorption time based on the data (black points) from the TPD experiments.

Significance

This study is focused on improving the fundamental understanding of ammonia synthesis. Improving the fundamental understanding of the reaction mechanism for ammonia synthesis is important as it can lead to identification of improved catalysts allowing for milder reaction conditions and therefore a more energy efficient process.

References

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