

Understanding the ammonia synthesis catalyst poisoning: laboratory experiments to enhance the reactors performances

M. Furlan¹, P. Biasi¹, J. D'Alessandri¹, C. Ferrini^{1*}

¹R&D Department, CASALE SA, Lugano, 6900, Switzerland

The catalytic ammonia synthesis from H₂ and N₂ is one of the most important industrial reactions. The catalyst is made from iron oxide with a little percentage by weight of other oxides added as promoters. Despite the improvement made in recent years the catalyst is still sensitive to the poisoning due to oxygenates compounds (CO, O₂ and H₂O). In normal industrial conditions, few ppm of oxygenates compounds can reach the ammonia synthesis reactor, and even if they are below 10 ppm they affect the iron catalyst life and performances^[1-2]. In this work we have investigated the influence of few ppm of oxygenates compound (O₂ and H₂O) on the poisoning behavior of ammonia synthesis catalyst. The understanding of the chemistry behind the effect of few ppm of oxygenates compounds in industrial reactors can reveal new insights on the ammonia synthesis reaction that will increase drastically the reactors' performances.

To investigate the poisoning effect, an ammonia industrial synthesis catalyst was used: firstly, crushed and then in its granular form to understand the intrinsic loss of activity and the one at real industrial conditions. Since it is well known that the poisoning by CO and CO₂ has the same effect of the H₂O and O₂^[1], the research was performed using only H₂O and O₂ with a ratio of 2.5:2.5 ppm. The experiments were performed in a fixed bed tubular lab scale reactor between 350°C and 450°C at a pressure of 100 bar. Different gas hourly space velocities (GHSV h⁻¹) were used to investigate the catalyst performances close to and far from the equilibrium conditions. The experiments consisted, after reaching the steady state conditions, in switching on/off the feed containing the oxygenates compounds. In this way the dynamics of the poisoning/cleaning effect were investigated. From the results obtained it was understood that a low amount of oxygenates compounds reversibly poisons the catalyst, even in a long time period. When the high purity of the gas mixture is restored the catalyst goes back to its original performances with no loss of activity. The temperature played a critical role, for example at 380°C the poisoning rate was faster compared to the one at 430°C. The cleaning rate was the opposite: the higher the temperature, the higher the oxygen desorption rate and thus the catalyst recovery. This information revealed that the oxygen desorption rate was faster at 430°C, indicating that the poison effect can be reduced when the temperature is increased. The data obtained were then compared with data from industrial reactors. A correlation between lab scale tests and data from industrial reactors was found. Start-up conditions of industrial reactors were found to be critical. The reduction of the poisoning effect in the reactors start-up conditions can enhance the life and performances of the catalyst. The ratios between poisoning and cleaning at different temperatures were compared and correlated with measurements of oxygen adsorption and desorption on the catalyst surface. The correlations found were then used to define the criteria to extend catalyst stability and life. Finally, the catalytic tests made with granules demonstrated how it is important to study also the catalyst "as it is fed" in the industrial reactors to achieve better performances in poisoning conditions.

In conclusion, the importance of understanding the poisoning and cleaning rate of the ammonia synthesis catalyst has been demonstrated. A procedure to evaluate the poisoning rate and degree for the industrial catalyst was identified. A correlation between lab experiments and data from industrial reactors was found and used to increase the reactors' performances. Moreover, the information can be used in the industrial reactors and extend catalyst life under industrial conditions.

[1] K.C. Waugh, D. Butler, B.E. Hayden, *Cat. Letters*, **1994**, 24, 197-210.

[2] B. Fastrup, H.N. Nielsen, *Cat. Letters*, **1992**, 14, 233-239.