Validation of the Iron Catalyst for green ammonia application

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Ammonia is a fundamental feedstock for both agriculture and energy sectors [1]. For this reason, the research of sustainable production of ammonia, replacing fossil fuels with green or zerocarbon, is fundamental for academia, industries and governments. Green ammonia (gNH3) production involves the use of green hydrogen in the Haber-Bosh process using renewable electricity [2]. Therefore, due to the nature of the renewable energy sources, it is crucial to precise characterize the converter functioning when undergoes fluctuations under operating conditions [3]. Moreover, also the behavior of ammonia synthesis catalyst must be verified, since its behavior at non-stationary conditions, is a missing information and no experimental evidences are currently available in the scientific literature. The goal of the present work is the assessment of the catalyst activity under accelerated green NH3 conditions, characterized by frequent oscillations of the main operating variables including catalyst bed temperature, pressure, space velocity, as well as changes in the inlet gas feed composition. This allows to achieve a deep understanding on how to use the current ammonia synthesis catalyst in green NH3 process. It is also very important to understand how to prevent abnormal catalyst behavior in these unexplored operating conditions. Indeed, robustness of catalyst over long-lasting applications during operations is not known yet and these information will have an impact on the understanding of operative costs.



Experiments were performed by varying the selected parameters as temperature, pressure and GHSV in cyclic alterations. Preliminary results of fast cycles of temperature in clean conditions reveals that the catalyst is stable. Moreover, the effect of oxygenated compound at the same conditions, was studied. After a first partial deactivation due to the poisoning effect of oxygenates, the ammonia productivity stabilizes, without any further decline in %vol. NH3. The loss in catalyst activity in presence of oxygenating compounds is proportional to the O content in the feed; higher the amount, higher the effect on iron catalyst. However, once the catalyst is submitted to clean syngas treatments at 450°C after poisoning, its catalytic activity results always restored. In addition, it was found that the recovery time is dependent on the O ppm content maintained during the "deactivation stage". Therefore, it can be concluded that cyclic alterations of the temperature combined with different atomic oxygen content in the syngas mixture do not cause a permanent and irreversible deactivation of the catalyst.

[1] L. Huazhang, *Chem. Industry Press*, **2013**.

[2] Sust. Energy Fuels, 5, 2814, **2021**.

[3] M. Ravi, and J.M. Makepeace, Chem. Sci., 890, 13, 2022.