Role of the iron and neodymium precursors on the performance of ammonia synthesis catalyst

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Highlights

- Nd_2O_3- supported Fe catalysts for NH_3 synthesis.
- Dependence of the active phase precursors on the catalyst performance.
- Superior NH_3 synthesis performance for the catalyst prepared with nitrates.
- Decrease activity for catalysts prepared from chlorides and sulphates.

1. Introduction

Ammonia synthesis is one of the most important chemical processes that requires demanding conditions: T = 400-500 °C, p = 15-30 MPa, and the usage of a catalyst. In industrial processes, two types of ammonia synthesis catalysts are used in plants. Staple, iron-fused catalysts are the most common, but also more active, specialised promoted-ruthenium catalysts are also used, albeit less often. Due to their susceptibility to poisons, the high cost of Ru, and the high energy consumption of the entire ammonia production process, new catalytic systems are continually sought as a replacement. [1] Since cost, availability, and reliability are the main factors determining catalyst choice, the recommended solution is to develop a novel, stable iron-based catalytic system, modified to achieve higher activity, e.g., by using a carrier. In this area, rare-earth metal oxides are attractive candidates. Primarily, they display high basicity, relating to their ability to donate electrons to the active phase, influencing the limiting-reaction step - the dissociation of the nitrogen molecule, which can accelerate the overall rate. One of the most promising carriers is neodymium oxide. [2,3] Research indicates that its use in ammonia synthesis improves catalyst properties and activity, but its price and lowered availability due to other uses hinder its widespread application. One strategy might be to use neodymium oxide derived from recycled materials as an alternative source. Although no technology is currently in use, research into recovering iron and neodymium from NdFeB magnets and their upcycling is rapidly advancing. [4] Using these elements from e-waste can improve the sustainability of the ammonia synthesis process, and properly designed catalytic systems can reduce energy consumption or increase productivity. A key consideration, however, is determining the most effective way to incorporate these elements into the system to ensure the sought-after properties.

2. Methods

This research aimed to investigate the role of used precursors in the preparation of catalysts for ammonia synthesis. Carriers were synthesized by the precipitation method using $Nd(NO_3)_3 \cdot 6H_2O$, $NdCl_3 \cdot 6H_2O$ and $Nd_2(SO_4)_3 \cdot 8H_2O$ as initial reagents. Additionally, commercial neodymium oxide was used as a reference material. Iron – active phase, was applied by the wet impregnation method using: $Fe(NO_3)_3 \cdot 9H_2O$, $FeCl_3 \cdot 6H_2O$, and $Fe_2(SO_4)_3 \cdot H_2O$ as initial reagents. The total amount of metal was set at 10 wt.%. The obtained samples were subjected to physicochemical characterisation using temperature-programmed techniques (H_2-TPR, H_2-TPD, CO_2-TPD), N_2 physisorption, X-ray diffraction (XRD), and scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDX). The activity of iron catalysts was tested for ammonia synthesis at 470°C under 6.3 MPa.

3. Results and discussion

Conducted studies revealed that precipitated supports were in the form of $Nd_2O_2CO_3$, which, in the reducing atmosphere, undergoes thermal decomposition to Nd_2O_3 and CO_2. The highest basicity was observed for the support prepared from neodymium nitrate. The thus-obtained catalyst (with iron and

neodymium from nitrate) achieved the highest number of adsorption centres for hydrogen and, together with a catalyst on a commercial carrier, achieved the highest activity in ammonia synthesis. The use of chlorides and sulphate precursors was reportedly associated with catalyst surface contamination, leading to the lowest ammonia reaction rates. Despite the effect being prominent, further research is required to investigate the deeper mechanisms of activity changes.

4. Conclusions

The type of precursors used strongly influences the catalyst's properties and activity in the ammonia synthesis reaction. The use of nitrate precursors has the greatest potential for preparing catalysts for ammonia synthesis. Chlorides and sulphates decrease the catalyst's activity due to their poisonous effects on the active phase. Appropriate catalyst design is crucial for achieving effective ammonia synthesis systems.

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