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Alloyed Ni-Fe nanoparticles as catalysts for NH_3 decomposition

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ABSTRACT

A rational design approach was used to develop an alloyed Ni-Fe/Al_2O_3 catalyst for decomposition of ammonia. The dependence of the catalytic activity is tested as a function of the Ni-to-Fe ratio, the type of Ni-Fe alloy phase, the metal loading and the type of oxide support. In the tests with high temperatures and a low NH_3-to-H_2 ratio, the catalytic activity of the best Ni-Fe/Al_2O_3 catalyst was found to be comparable or even better to that of a more expensive Ru-based catalyst. Small Ni-Fe nanoparticle sizes are crucial for an optimal overall NH_3 conversion because of a structural effect favoring the smallest particles in terms of catalytic activity per active site. Compared with SiO_2, ZrO_2 and TiO_2, the support materials Al_2O_3 or Mg-Al-spinel give the highest performance in the high temperature range.

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1. Introduction

Hydrogen can be used as an environmentally clean energy carrier to power for example fuel cells and internal combustion engines [1]. However, serious challenges related to hydrogen as energy vector, such as the development of safe infrastructures for hydrogen storage and distribution must be addressed. In this relation, NH_3 has a number of favorable attributes, the primary one being its high capacity for H_2 storage [2,3], and that NH_3 can be safely stored in salts such as $MgCl_2$ with a high density of H_2 compared to liquid H_2 [4]. Ammonia is the second largest chemical in terms of production volume. More than 130 million tons of NH_3 is produced each year, bulk of which is used as fertilizer and the infrastructure for transport of NH_3 in large scale already exists [2].

To be able to use H_2, stored in NH_3, it is necessary to decompose the NH_3 into H_2 and N_2, and this is done most efficiently by using a catalyst [5]. The most active catalysts for NH_3 decomposition are based on noble metals like Ru, Rh, Pt, Ir as well as the non-noble metals Ni and Fe [6–13]. The catalytic performance of these metals is typically enhanced by distributing the metals on a high surface area support material, such as an oxide [6,7,10–13] or carbon-based material [6–9,12,13]. The catalytic activity may further be enhanced by the use of promoters such as K, Na, Li, Ce, Ba, La, Ca, Cs [6,7,9–13].

Theoretical models, describing the activity of catalysts for ammonia synthesis as a function of the N_2 dissociative chemisorption energy for transition metals in so-called volcano plots [14], have been shown to be applicable to the ammonia decomposition reaction as well [15]. The volcano plot presents Ru near the top of the curve, as indicated by Fig. 1 which is reprinted from Ref. [15]. Ni and Fe are less catalytically active and are found to the right and left side, respectively, of Ru in the volcano plot (Fig. 1). The shape of the volcano plot implies that there is an optimum for the adsorption energy, which reflects the compromise that a good catalyst should be able to activate the reactants, but not bind the reaction intermediates and products too hard. Previous studies have used a rational approach to design catalysts, where the idea was to combine metals with high and low binding energies to obtain an alloy with optimal interaction strength, resulting in a high catalytic activity [16]. For the ammonia synthesis reaction a Co-Mo-based catalyst with a relatively high activity was designed by using this approach [16]. Similarly, a highly active ammonia decomposition catalyst could possibly be developed by alloying metals from both sides of the peak of the volcano curve (Fig. 1), e.g. Ni and Fe. A few alloys have already been developed as catalysts for NH_3 decomposition, for example related to NO_x emissions in fossil-fuel fired power plants [17], but also related to the conversion of NH_3 into H_2 [18–20]. These are, however, only described in patents from which the exact alloy composition and the catalytic performance is not fully transparent.

A factor that complicates the approach of finding an alloy with an optimal peak position in the volcano plot, is that the peak position depends on the reaction conditions [5,15]: for high NH_3-to-H_2 ratios (e.g. 99% NH_3) the peak position is between the nitrogen binding energies for Ru and Ni, while a decrease in the

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