



A method of determining nanoparticle size distribution in iron ammonia synthesis catalyst by measuring mass changes during the nitriding process



Rafał Pelka*

The West Pomeranian University of Technology, Szczecin, Poland, The Institute of Chemical and Environment Engineering, 10 Pułaskiego Street, Szczecin 70-322, Poland

ARTICLE INFO

Article history:

Received 31 March 2016

Received in revised form 2 August 2016

Accepted 9 September 2016

Available online 16 September 2016

Keywords:

Heterogeneous catalysts

Nanocrystalline iron ammonia synthesis catalyst

Nanoparticle size distribution

Nitriding process

Nanomaterials

Phase transition

ABSTRACT

A new method for determination of nanoparticle size distribution, on the basis of measurements of nanomaterial conversion degree as a function of the chemical potential of gas reagent, was presented. The method was applied for determination of nanocrystallite size distribution in a pre-reduced iron catalyst for ammonia synthesis being an example of a nanomaterial. Samples were reduced with hydrogen at 500 °C and then nitrided at 300 °C in gaseous ammonia-hydrogen mixtures of different nitriding potentials. Conversion degree measurements, viz., measurements of mass changes of the catalyst were performed in a differential reactor equipped with systems that enable thermogravimetric measurements and analysis of gas phase chemical composition. Based on the performed measurements, a relationship binding the conversion degree with size distribution was proposed. The resulting size distribution of nanocrystallites was compared to distributions determined by known techniques based on XRD or on measurements of the nitriding reaction rate. The size distribution determined using the new method has a higher resolution, revealing more details of the sample morphology.

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1. Introduction

One of the still unresolved challenges in chemistry is the efficient utilization of molecular nitrogen in the production of nitrogen-containing compounds. The use of nitrogen as a feedstock is highly appealing for industrial applications, as it is abundant, easily accessible and inexpensive. However, one of the barriers is the inertness of nitrogen, since it is a simple triply-bonded diatomic molecule that is very difficult to activate (ionization potential 15.058 eV; negative electron affinity -1.8 eV; bond dissociation enthalpy 945 kJ mol^{-1}). In fact, only one commercially successful process utilizes N_2 as a reagent [1–4] – the Haber–Bosch process in which the reaction of dinitrogen with dihydrogen over a promoted iron- or ruthenium-based catalyst is involved to produce ammonia. Catalysts for the synthesis of ammonia, including iron catalyst, were the subject of studies related to the determination of the mechanism of ammonia synthesis and decomposition [2,5–7]. In the course of these studies it was determined that due to the

nanocrystalline structure of the catalyst the determination of size distribution of the nanocrystallites is crucial to correctly identify the properties of a Fe– NH_3 – H_2 system. In addition, an iron catalyst was used as a model system to study the nitriding process [8].

The study of the kinetics of chemical reactions in the process of nanocrystalline α -iron nitriding with ammonia, aiming to develop a model of reaction between nanocrystalline materials and a gas phase with the formation of solid and gas products, was carried out in the area where the nitriding potential $P = p_{\text{NH}_3}/p_{\text{H}_2}^{3/2} \gg P_0$ (P_0 – the minimum nitriding potential, at which the phase transition of each nanocrystallite of certain size begins) and in the temperature range of 300–500 °C. At these high temperatures, the rate of diffusion inside the crystallite is greater as compared with the surface reaction rate (the nitriding process rate is limited by the rate of the processes occurring on the surface of nanocrystallites) and therefore there occurs a state in which the concentration gradient in the volume of the crystallite is not present. Consequently, α -iron nanocrystallites undergo a phase transition to γ '- Fe_4N nitride in their entire volume in the order of their size from the smallest to the largest after exceeding the critical concentration of nitrogen in α -iron [9,10].

As a result of these studies, two chemical methods for determining the size distribution of iron nanocrystallites were developed.

* Correspondence to: The Institute of Chemical and Environment Engineering, 10 Pułaskiego Street, 70-322 Szczecin, Poland.
E-mail address: rpelka@zut.edu.pl

The first method involves XRD technique and uses measurement results of the average crystallite size (of the substrate or the product) corresponding to given conversion degrees, α [11]. Then, from the dependence of the average nanocrystallite size of substrate or product on the conversion degree, it is possible to determine the crystallite size distribution. The second way is based on measuring the chemical reaction rate in solid phase and is, therefore, limited to systems where a reaction between nanocrystalline materials and a gas phase occurs [12]. It was possible to determine the changes of mass distributions resulting from iron nanocrystallites annealing at temperatures above 500 °C [13]. Due to the link existing between mass distribution function of crystallites and the rate of nitriding reaction, it was also possible to determine the shapes of relative crystallite mass distributions. Both methods rely on the relationship between the conversion degree and specific physical properties.

The nitriding degree dependence on the nitriding potential and temperature for bulk or coarsely-grained substances is commonly known as Lehrer's diagram [14]. At a given temperature, phase transitions occur at a specific, constant nitriding potential. In the case of nanocrystalline materials, discrepancies with Lehrer's diagram are observed [15–17], and the phase transition point of a sample depends on the nitriding potential. The maximum concentration of nitrogen in a volume of iron nanocrystallites, X_b^{\max} , at which the step change in thermodynamic parameters associated with the phase transition takes place, corresponds to a predetermined value P_0 . The composition of binary systems at given pressure and temperature is clearly determined by the Gibbs' phase rule. In the case of nanomaterials, the impact of nanoparticle size on the properties of nanomaterials must also be taken into account.

It was determined [18–21] that in the nitriding process of iron ammonia synthesis catalyst with hydrogen-ammonia mixtures of increasing nitriding potential at a constant temperature the steady states at a given nitriding potential, P^a_0 , were set up.

In stationary states, the reaction rate in the solid phase equals zero at $P = P^a_0$, and certain fixed maximum levels of nitriding degree, α , are observed as a function of P_0 , and the chemical potential of nitrogen remaining in the volume of iron is equal to the chemical potential of nitrogen in the gas phase. The parallel reaction of catalytic decomposition of ammonia proceeds at a constant rate. Under these conditions, a solution of nitrogen in α -iron nanocrystallites exists simultaneously with nanocrystallites that already have been converted to γ' nitride phase. Both types of nanocrystallites (α -Fe and γ') have a different nitrogen content, approx. 0.1 wt% and 5.7 wt% [22], respectively, wherein these values are a function of temperature. The nitriding degree of a sample containing nanocrystallites of different sizes increases with the nitriding potential. On the basis of X-ray studies it was found [16,20] that both the minimum potential, P^a_0 , at which the phase transition of all nanocrystallites with specific sizes begins and iron nitriding degree depend on the crystallites size. It was observed that the smaller the crystallite, the greater the value of the nitriding potential of the gas phase is required to start the phase transition of this crystallite from α -iron phase to γ' -Fe₄N. Consequently, along with an increase of the nitriding potential and nitriding degree, decreasingly smaller iron nanocrystallites (of progressively smaller volumes) underwent the phase transition. Numerical modeling of nanocrystalline iron nitriding with NH₃/H₂ mixtures was carried out. Calculation results confirmed the existence of the phenomena observed experimentally [23].

Catalysis is especially important in everyday life [1,2,5,24–27]. Thus it is very important to have a better understanding of the structure and properties of catalysts, which very often contain nanoparticles as active species. In many industrial processes it is essential to accurately determine particle or grain size distributions (GSDs). GSD determination has also become the fundamental

measurement when dealing with nanomaterials, due to the fact that their physical (e.g. electromagnetic wave absorption, magnetic characteristics, melting temperature) and chemical (e.g. catalytic activity and selectivity, formation of new materials) properties depend on the size of nanoparticles [23,28–35]. Therefore, determining the average size of grains only – as a parameter characterizing the material – is insufficient and complete characterization should include the grain size distribution. Furthermore, understanding nanometal-adsorbate interactions is crucial to controlling and improving the functionality of metal nanoparticles. Adsorption depends on the morphological characteristics of the nanoparticles (their size and shape). On the other hand, chemical environment (presence of adsorbates) determines the morphology of nanoparticles [32]. Therefore, the advanced procedures of obtaining of nanoparticles take into account morphology effects on adsorption. These procedures enable the rational design of nanomaterials with tailored properties in applications ranging from catalysis to drug delivery.

In this respect, there is a need for the method of accurate determining the size distribution of nanoparticles which takes into account both surface phenomena (like adsorption) and changes in the reaction conditions during the actual process. In this paper, based on the statements presented above, a chemical method for determining the size distribution of nanoparticles is presented. In this method, in the stationary states, the variations in the conversion degree, corresponding to values of the chemical potential of a gas phase, are recorded and the relative size distribution is determined. After determining the size of the smallest or the largest nanoparticles (e.g. by SEM, TEM), or the average crystallite size (e.g. by XRD) or specific surface area (e.g. by BET) the method proposed hereby enables to determine the real size distribution of nanoparticles.

2. Methodology

Activation of the nitrogen molecule occurs on the surface of the iron catalyst. Assuming a uniform chemical composition of the surface of crystallites, the active surface of the catalyst depends on the size distribution of nanocrystallites. Therefore, in any study of the activation of nitrogen the catalyst should be described in terms of GSD as well. Otherwise, due to the inhomogeneity of catalytic material [36], the study based on classical methods can lead to erroneous results. The nitriding reaction of iron ammonia synthesis catalyst was studied as a nanocrystalline substance – gas phase system.

In nitriding process, the chemical equilibrium between a nanocrystalline substance and gas phase holds [16–21]. Chemical potentials of nitrogen atoms in the gas phase, μ_g , of nitrogen chemisorbed on the solid surface, μ_s , and dissolved in a volume of iron nanocrystallites, μ_b , are equal to each other:

$$\mu_g = \mu_s = \mu_b \quad (1)$$

The reaction rate of iron nitriding with ammonia is a function of ammonia concentration in the gas phase, $r = f(p_{\text{NH}_3})$. Arabczyk et al. [37] determined the minimum concentration of ammonia at which the nitriding reaction occurs. If instead of ammonia concentrations we use the concept of nitriding potential, the nitriding reaction rate, r , can be expressed with the following formula [8]:

$$r = kf(\alpha)(P - P_0) \quad (2)$$

where: k – reaction rate constant.

At stationary states $r = 0$ when $P = P_0$.

In the first step of the proposed procedure for determining the size distribution of nanoparticles or nanocrystallites the relationship $\alpha = f(P_0)$ is to be experimentally determined. As can be concluded from experimental observations concerning nanocrystalline iron nitriding process, with increasing nitriding potential,

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