



# Microwave-assisted ammonia decomposition reaction over iron incorporated mesoporous carbon catalysts



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## ARTICLE INFO

### Article history:

Received 29 April 2016

Received in revised form 11 August 2016

Accepted 16 August 2016

Available online 17 August 2016

### Keywords:

Microwave

Ammonia

Hydrogen

Mesoporous carbon

Iron oxides

## ABSTRACT

Microwave-assisted ammonia decomposition reaction was investigated to produce CO<sub>x</sub> free hydrogen, for fuel cell applications. Iron incorporated mesoporous carbon catalysts were prepared at different metal loadings, following an impregnation procedure. Mesoporous carbon acted as the catalyst support, as well as the microwave receptor. Complete conversion of ammonia was achieved at 450 °C over the catalyst having 7.7 wt% Fe, when the reaction was carried out in the microwave reactor system, using pure ammonia (GHSV of 36000 ml/h g<sub>cat</sub>). However, in the case of using the conventionally heated reactor, complete conversion of ammonia was achieved only at 600 °C. Iron oxides, namely maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite (α-Fe<sub>2</sub>O<sub>3</sub>) simultaneously appeared in the structure of the synthesized catalysts, after their calcination at 450 °C, under pure N<sub>2</sub> flow. Iron oxides present in the calcined catalytic materials then were reduced to metallic iron at 500 °C. Formation of iron carbide crystals was observed in the structure of spent catalysts that were used in microwave reactor system, while metallic iron crystals were still present in the catalysts that were tested in conventionally heated system.

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## 1. Introduction

In recent years, ammonia has been considered as an important raw material for hydrogen production, since conventional routes, such as steam reforming, result in formation of CO<sub>x</sub> components besides hydrogen. These byproducts cause a decrease in fuel cell performance due to their poisoning effect [1,2]. Sources of ammonia can be either in liquid or solid form. Generally known, ammonia is a valuable chemical that can be commonly used in different industrial processes to produce fertilizers, animal feed and to manufacture explosives, paper, rubber etc [3]. At ambient temperature and pressure, ammonia is present in gaseous form. It can be easily liquefied at 298 K under the pressure of about 10 bar and can be stored in relatively inexpensive pressure vessels [4]. However, under ambient conditions it has malodorous and it is harmful and may damage human health and environments [3]. During the production of ammonia and urea, excessive amount of ammonia is being emitted to the atmosphere or discharged with wastewater effluent streams which cause water pollution problem as well as loss of raw materials. It should be pointed out that acceptable

ammonia and urea level for wastewater of urea plants should be lower than 10 ppm for both of them. So removal and recovery of ammonia from wastewater is important [5,6]. Different methods such as biological processes, ion exchange, micro-wave plasma discharge, water scrubbing, air stripping, electrochemical oxidation have been applied for the treatment of ammonia removal. These kind of processes generally involve a phase transformation and result in contaminated sludge. Therefore adsorbent require further disposal and their maintenance and operation are costly [7,3]. Recently decomposition reaction has been proposed to decrease ammonia concentration in waste water since it produces CO<sub>x</sub> free hydrogen which is one of the highly promising alternative energy sources [5,3].

Ammonia decomposition reaction has been studied using a number of catalysts. Ruthenium is known to be the most active metal among single metals and various studies have been carried out using ruthenium with different supports [8–12]. In order to commercialize the production of CO<sub>x</sub> free hydrogen production from ammonia, studies on the preparation of highly active catalysts using much cheaper metals, such as Ni [2,13,14], Fe [9,13,15–17], Co [18,19] have been performed by different research groups.

Microwaves are present between infrared radiation and radiowaves in the electromagnetic spectrum. They have wavelengths between 0.001 and 1 m and the corresponding frequencies

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are between 300 and 0.3 GHz. They are generally used in telecommunications and radar transmissions. In domestic microwave ovens, which are used for food processing and industrial microwave applications for chemical synthesis, a microwave frequency value of about 2.45 GHz is used, in order to avoid any interference with telecommunication microwaves [20,21]. Nowadays, microwave energy is used as an alternative heating method to enhance heterogeneous chemical reactions, for either endothermic or exothermic ones. Unlike conventional heating methods, heat is generated by direct conversion of electromagnetic energy [22,23]. Indeed, the interaction of charged particles in a material with the electric field component of electromagnetic radiation, i.e. microwave frequency waves, resulted in the material to heat up [20]. So, heating from interior of the material occurs [22,23] and better energy utilization is obtained [24]. Since selective, volumetric, uniform and non-contact heating occur in microwave focused reaction systems, rate enhancement, higher yields and improved selectivities can be obtained [22,23,25–27]. Lower coke formation and highly stable performance during the reaction were also reported for microwave systems [24]. Less time is required for heating in the reaction medium [28]. Unlike the conventional systems, less energy input for heating was also discussed in the literature [29]. Other advantages of using microwave heating system are (i) a greater control of heating process, (ii) quick start and stop facility, (iii) high level of safety and automation and (iv) reduced equipment [22,23,28]. Microwave heating has been applied in a variety of chemical reactions, such as pyrolysis of coffee hulls to hydrogen rich fuel gas [28], CO<sub>2</sub> free hydrogen production by methane decomposition [22], pyrolysis of methane to hydrogen [30], growth of nanofilament from methane [26], dry reforming of methane [31], biodiesel production from soybean oil [29], methanol autothermal reforming [32], steam gasification of process of biochar [25], steam reforming of ethanol [27], and methanol [33], water gas shift reaction [34], pyrolysis of coal [35] and pyrolysis of rice straw for hydrogen production [36]. Although different studies are reported for hydrogen production, an application of microwave reactors for the ammonia decomposition reaction is missing in the literature.

In order to absorb microwave energy, a dielectric material should be used in the reactor system [24]. However, not all of the materials have the ability to absorb microwave. Dielectric loss tangent is used for explaining the ability of a material to be heated in the presence of microwave and it is calculated using dielectric constant, i.e., a measure of how much incident energy is absorbed and dielectric loss factor, i.e., a measure of dissipation of electric energy in the form of heat [20]. Carbonaceous materials are known as strong absorbers of microwave, considering their dielectric loss tangent values. They have the ability of converting microwave energy to thermal energy which results in an increase in temperature [31,20,35]. When carbonaceous materials are used as a catalyst in a reaction medium, they act not only as a catalyst but also as a microwave receptor in this medium [31]. If the catalyst is transparent to microwave, carbonaceous material is used as a receptor together with the catalyst to enhance the reaction [20].

In the present study mesoporous carbon is selected as the carbonaceous material which will act as a catalyst support and also a microwave receptor and iron is used as the active component of the catalyst for ammonia decomposition reaction. Different studies on iron incorporated mesoporous carbon catalysts have been reported for different reactions, due to the superior properties of mesoporous carbon, such as high chemical stability, good thermal conductivity, weak metal-carbon interaction, large pore size and uniform pore structure [37–40]. Minchev et al. [37] prepared iron oxide modified CMK-n type mesoporous carbon catalysts by wet impregnation procedure and used in methanol decomposition reaction. Li et al. [38] prepared Fe-containing mesoporous carbon materials following a soft templating route and tested in the cat-

alytic wet peroxide oxidation of phenol. Duan et al. [39] prepared ordered mesoporous carbon supported iron catalysts by an incipient wetness impregnation procedure to be used in Fenton-like degradation of 4-chlorophenol. Cruz et al. [40] synthesized iron based polymeric mesoporous catalysts for Fischer-Tropsch synthesis using wet impregnation procedure. An application of iron incorporated mesoporous carbon catalysts for ammonia decomposition reaction is limited in the literature. Lu and coworkers [15] prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> supported on CMK-5 which was a bimodal mesoporous ordered carbon by impregnation procedure. They reported complete conversion of ammonia at 700 °C and space velocity of 60000 cm<sup>3</sup>/h g<sub>cat</sub> over these catalysts in the conventional system.

In the present study hydrogen production from ammonia was investigated in a focused microwave heated system over the iron incorporated mesoporous carbon catalysts and the results were compared with the corresponding results obtained in a conventionally heated tubular reactor.

## 2. Experimental

### 2.1. Catalyst preparation

Iron incorporated mesoporous carbon catalysts were prepared following an impregnation procedure. Commercially available mesoporous carbon (99.95% purity, Sigma Aldrich) was used as a support material. It was selected due to its ability to act as a microwave receptor in converting electromagnetic energy into heat. Iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Sigma Aldrich) was used as a metal precursor and catalysts were prepared adjusting Fe wt% in the synthesis solution being between 5 and 15. A mixture was prepared solving 0.5 g of carbon source in a 5 ml of ethanol solution (vol 20%). Then, ethanol solution of iron precursor was added into this mixture in a dropwise manner. The final solution was stirred at 60 °C with a rate of 280 rpm for 3 h and then it was kept at 80 °C for 10 h, until complete drying. Finally, the obtained sample was calcined under the flow of nitrogen (60 ml/min) at 450 °C for 5 h. Catalysts were called as Fe@MC(X), where X referred to the weight% of Fe to the mixture of Fe and mesoporous carbon, in the preparation of synthesis solution. Calcined catalysts were reduced just before each experiment under the flow of pure hydrogen at 500 °C.

### 2.2. Catalyst characterization

Different techniques were applied in order to characterize the synthesized catalysts. Thermal analysis (TGA-DTA) was performed using Perkin Elmer Pyris 1 Instrument, with a heating rate of 20 °C/min, under the flow of nitrogen, with a flow rate of 100 ml/min. It was used to determine the appropriate temperature for calcination process. Temperature programme reduction (TPR) experiments were carried out using Chembet-3000 instrument. Prior to the analysis, the sample was firstly degassed at 150 °C under the flow of pure He during 1 h, and then cooled to room temperature. Reduction was performed from room temperature to 800 °C under the flow of 5% H<sub>2</sub> in nitrogen. Inductively coupled plasma (ICP) analyses were carried out by Perkin Elmer DRC II model ICP-OES equipment to measure the exact metal content of the synthesized catalysts. Nitrogen adsorption-desorption analyses were carried out at 77 K, using the Quantachrome Autosorb-6B instrument, after the samples were degassed at 200 °C for 3 h. The surface area was calculated using the Brunauer, Emmett and Teller (BET) method and pore size distributions were calculated by applying the BJH method to the desorption isotherm. Powder X-Ray diffraction (XRD) analyses were performed by a BRUKER-AXS D8 ADVANCE A 25 diffractometer with a Cu K $\alpha$  radiation source, operated at 40 kV voltages and 40 mA current. The diffractograms

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