



## Short communication

## Ambient pressure synthesis of ammonia using a microwave reactor

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## ABSTRACT

Ammonia synthesis processes that can operate at low temperatures and pressure and have ability for small-scale distributed production are of interest. Microwave assisted synthesis has shown improvements in kinetics and does not have economy of scale limitations of the Haber-Bosch process. A microwave reactor was used to produce ammonia at temperatures from 300 to 500 °C. Three catalyst systems were compared: commercial Fe catalyst, and supported Ru/Al<sub>2</sub>O<sub>3</sub>, and Fe/Al<sub>2</sub>O<sub>3</sub> catalysts. The ammonia production of the dispersed catalysts was significantly higher than the commercial catalyst with maximum production of 128 μmol/g/h at 300 °C. This increase in production is attributed to an optimal electron movement under the microwave field.

## 1. Introduction

Ammonia is the second most abundant synthetic chemical produced today mainly by the Haber-Bosch process and consumes between 1 and 2% of the total energy supply in the world [1]. This synthesis reaction is typically carried out at temperatures between 400 and 500 °C, pressures above 100 bar and is efficient at large scale [2, 3]. These large-scale plants require considerable energy and water resources and a distribution infrastructure to get the products to consumers. If the ammonia synthesis could be scaled down the plants could be located more remotely for instance closer to crop sites and could take advantage of renewable energy resources. The ideal way to scale the ammonia synthesis process would be to remove the need for high pressure and lower the reaction temperature.

There are three major nonconventional processes being researched to activate nitrogen at low pressure/low temperature during ammonia synthesis: electrochemical, plasma, and electromagnetic routes. Although a large effort is being placed on the electrochemical approach, it has issues with low ammonia yields and poor efficiencies that will have to be overcome [4–6]. Non-thermal plasmas have been studied as an alternate reaction route to breaking the N<sub>2</sub> bond into active radicals. While this method is promising, there are difficulties with maintaining plasmas at atmospheric pressures efficiently. Adding a catalyst to the system is challenging, and the ammonia yields are low in comparison with other methods [7–9].

Electromagnetic radiation in the form of microwaves has become a focus for chemical synthesis in recent years due to the increased

selectivity and decrease in reaction times and temperatures [10–12]. Microwaves have the unique ability to selectively heat the catalyst and/or active sites which allows the reaction to occur at lower bulk temperatures. Microwaves have also been shown to decrease the activation energy needed for the reaction and hence shift the equilibrium to more products and/or different selectivity in products. Reactions and heating will be different between bulk catalyst and dispersed catalyst with dispersed catalyst being able to take advantage of the selective heating that microwaves offer.

This study tested a commercial Haber-Bosch catalyst that will be considered a bulk iron system with two supported metal catalysts. Fe and Ru were chosen due to their high activity for ammonia production. The iron catalyst was developed and tested as a lower cost alternative to the common Ru-based catalyst and to test a hypothesis of electron movement through the material systems. This is the first known reporting of ammonia synthesis by a non-plasma microwave system at atmospheric pressure.

## 2. Experimental

## 2.1. Catalyst synthesis

Commercial Haber-Bosch iron based catalyst was obtained from a commercial supplier (not identified upon request of supplier). Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, 99.9%), ruthenium(III) nitrosyltrinitrate (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, Ru 31.3%), and iron (II, III) oxide (Fe<sub>3</sub>O<sub>4</sub>, 99.9%) were purchased from Alfa Aesar and were used without any further

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purification.

Conventional incipient wetness impregnation was used to prepare Ru catalysts. Typically, anhydrous  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  salt corresponding to 4 wt% Ru loading was dissolved in deionized water and was added dropwise to  $\text{Al}_2\text{O}_3$  support. The powder was mixed using a mortar and pestle for 15 min before drying it at 105 °C overnight. The powder was then calcined in air at 500 °C for 4 h.

A 20 wt% Fe catalyst was produced by solid-state mixing of iron (II, III) oxide with alumina. The powders were ball milled overnight and calcined in air at 500 °C for one hour.

## 2.2. Catalyst characterization

Powder X-ray diffraction analysis was performed on a Panalytical X'pert Pro (PW3040) X-ray diffraction system utilizing  $\text{Cu K}\alpha$  radiation. Samples were placed on a zero diffraction Si holder and were scanned from 5 to 70° (2 $\theta$ ). Analysis was carried with Highscore Plus Analysis software equipped with a standard ICDD X-ray diffraction database supplied by Panalytical.

## 2.3. Microwave reactor

Microwave experiments were performed using a 2.45 GHz (2 kW) magnetron powered single mode microwave cavity from Sairem (model GMP20K, Neyron Cedex, France). The schematic of the MW reactor is provided in Fig. 1.

The reactions were carried out using the temperature controlled mode with maximum power set at 300 W. This mode allows for the power to be pulsed to maintain the set temperature. A quartz tube reactor with a 14 mm internal diameter was placed inside the microwave cavity. The temperature was measured using a laser-aimed IR pyrometer from Micro-Epsilon (model CTLM3, Ortenburg, Germany), with a temperature range from 200 to 1500 °C. This pyrometer setup allowed for the temperature reading from the side of the sample surface. Typically, 2 g of catalyst was used for each reaction while flowing a 3:1 stoichiometric mixture of hydrogen and nitrogen with an Ar trace (99.999%, UHP, Butler Gas) at a fixed flow rate of 100 sccm through the quartz tube. Reduction of the catalysts were carried out in the microwave at 250 °C for 2 h at 300 W for the Ru based catalyst and 500 °C for 2 h at 300 W for the Fe based catalyst with the synthesis gas flowing at 100 sccm. Ammonia synthesis tests were conducted from 300 °C and 500 °C and held at steady state for 30 min at each testing temperature.

## 2.4. Product analysis

All reactants and products ( $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ) gases were analyzed online using a 200 amu scanning magnetic sector mass

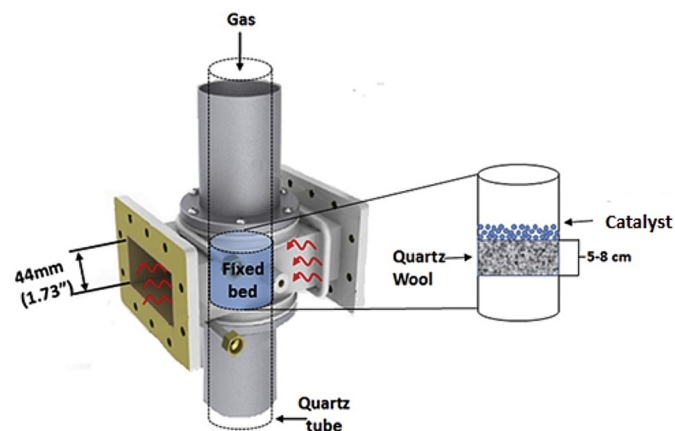


Fig. 1. Schematic of flow-through microwave reactor. Powder placed within the fixed bed region and held in place with quartz wool.

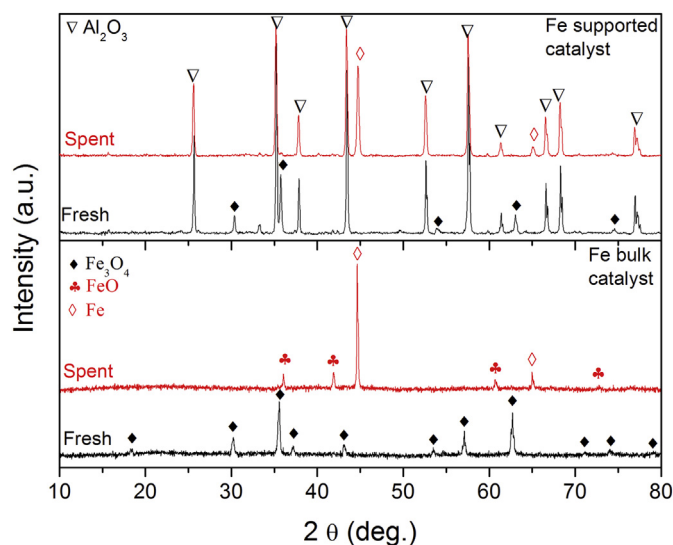


Fig. 2. XRD of the fresh and spent bulk HB catalyst and the supported Fe catalyst.

spectrometer from Thermo, model Prima BT Benchtop MS and an Agilent 3000A Micro GC equipped with a TCD detector and four columns: molecular sieve 5 Å, Plot Q, Plot U, and Alumina. The ammonia production was represented as  $\mu\text{mol}$  of ammonia produced per gram of catalyst per hour and was calculated using the average ppm recorded by the GC.

## 3. Results and discussion

The crystallinity of iron based catalysts, the commercial Harbor Bosh (HB) and supported Fe catalysts, were studied before and after the reaction. Fig. 2 showed the XRD patterns of these catalysts. The results revealed that the fresh bulk Fe catalyst (HB) is mainly composed of magnetite ( $\text{Fe}_3\text{O}_4$ ) with no other mixed oxide phase that could be observed. After microwave irradiation, under a reductive reaction mixture of  $\text{H}_2$  and  $\text{N}_2$ , almost a complete reduction was observed. Mainly, metallic Fe with some FeO crystalline peaks were identified, which could be due to handling the spent catalyst under air. Similarly, the supported Fe catalyst was fully reduced from  $\text{Fe}_3\text{O}_4$  to metallic Fe after microwave irradiation under same reaction gases. The average iron crystallite size was calculated from Debye Scherrer equation for bulk HB and supported catalysts and was found to be 31.2 and 34.0 nm for fresh and 65.8 and 30.5 nm for spent bulk and supported Fe catalysts, respectively. In general, crystallite size did not grow for the supported Fe catalyst after the reaction, possibly due to difference in heat transfer mechanisms between supported and bulk iron catalyst. Supported iron particles could possibly dissipate some of the localized microwave heating into the alumina support at a faster rate compared to bulk iron particles based on differences in the dielectric properties between the catalyst and support. These results agree with the observed high reflected microwave power during ammonia synthesis for supported iron catalyst compared to bulk iron catalyst.

Fig. 3 illustrates the XRD of fresh and spent supported Ru catalyst. The  $\text{RuO}_2$  crystalline phase peaks were observed along with broad amorphous peaks corresponding to gamma alumina support at  $2\theta = 45.6$  and  $67.3^\circ$ . Similarly, a microwave-assisted reduction of this catalyst was observed, where supported  $\text{RuO}_2$  particles were reduced into metallic Ru. Interestingly, a partial phase transformation from gamma to alpha phase of the alumina support was observed after microwave irradiation. This could be due to the selective heating of acidic polar OH groups in gamma alumina [13] followed by dehydration reactions and structural reorganization leading to a new active interface between metallic Ru catalyst and crystalline alpha alumina support.

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