

# TUNING THE FE/CNFs STRUCTURE FOR CATALYTIC AMMONIA DECOMPOSITION

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## Summary

The structure of the Fe/CNFs catalyst, which including the shape of Fe particle and the way it is supported on CNFs, is tuned by controlling the mechanism of CNFs growth to obtain a highly active and stable Fe catalyst for  $\text{NH}_3$  decomposition.

## Keywords

Fe-mica/CNFs; Iron nitride; Core-shell; Ammonia decomposition

## Introduction

Hydrogen-based proton-exchange membrane fuel cells (PEMFC) show good potential for the production of electricity.<sup>1</sup> The option of producing hydrogen directly from carbonaceous substances is limited by the low concentration of CO which degrades the PEMFC performance. As an alternative route,  $\text{NH}_3$  decomposition is particularly preferred as an attracting and promising route for the production of  $\text{CO}_x$ -free hydrogen, for its single feed stream, simplicity of start-up, and low overall device weight and volume.

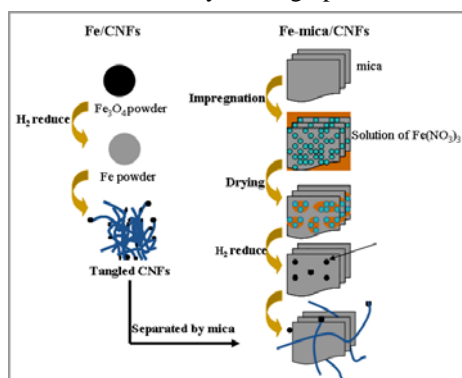
Traditional commercial catalysts for  $\text{NH}_3$  decomposition are based on Fe or Ni. Although a number of highly active catalysts have been continuously reported, their high metal loading and complicated synthesis route are the major obstacles for commercialization. Ru is the most active metal for this reaction. However, the large scale application of Ru-based catalysts seems to be prevented by the limited availability and high price of Ru.<sup>2</sup> Commercial

CNTs with residual Co- and Fe-nanoparticles are proved to have superior catalytic properties with respect to the reactivity as compared with the reported Fe catalysts.<sup>3</sup>

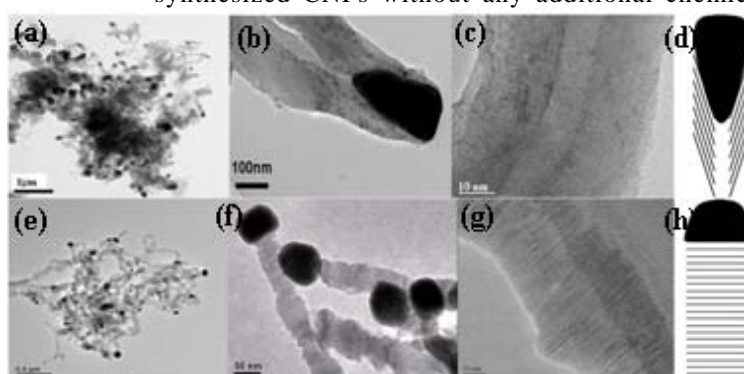
In this communication, Fe/CNFs catalyst is synthesized and the structure of the catalyst, which including the shape of Fe particle and the way it is supported on CNFs, is tuned by controlling the mechanism of CNFs growth to obtain a highly active and stable Fe catalyst for  $\text{NH}_3$  decomposition.

## Experimental

Following the procedures shown in Figure 1, CNFs with fishbone and platelet types (Figure 2c and g) of the microstructure were prepared in a fixed-bed quartz reactor by CCVD using CO as carbon source and nanoparticles of Fe and Fe/mica, respectively, as the catalysts. The as-synthesized CNFs without any additional chemical



**Figure 1.** Scheme of synthesis routes to Fe/CNFs and Fe-mica/CNFs composite.



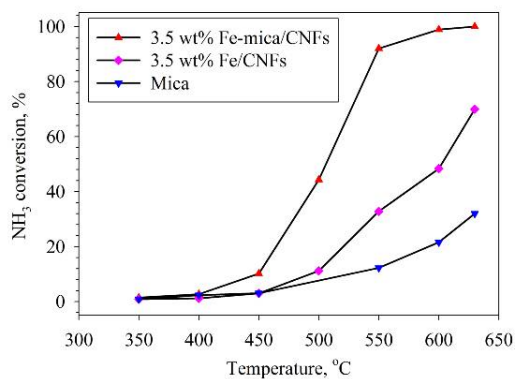
**Figure 2.** HRTEM images of Fe/CNFs (a-c) and Fe-mica/CNFs (e-f); A possible growth mechanism of Fe/CNFs (d) and Fe-mica/CNFs (h).

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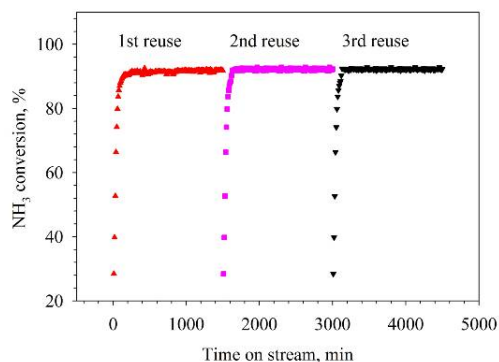
treatment were used as catalysts for  $\text{NH}_3$  decomposition. Product  $\text{N}_2$  and unconverted  $\text{NH}_3$  in the effluent gas were analyzed at room temperature by an online gas chromatography (GC) with a thermal conductive detector (TCD) and a 3 m Poropak Q packed column using  $\text{H}_2$  carrier gas. No signals corresponding to  $\text{CH}_4$  due to methanation of carbon could be detected by the GC.  $\text{NH}_3$  fractional conversion was calculated by a standardized method on nitrogen atom basis.<sup>1</sup> All experiments were carried out at atmospheric pressure.

## Results and discussion

As shown in Figure 2 a, b, e and f, size distributions of these residual Fe particles in Fe/CNFs and Fe-mica/CNFs are 50-300 nm and 40-60 nm, respectively. A possible growth mechanism of Fe/CNFs and Fe-mica/CNFs is proposed, which is in line with Baker.<sup>4</sup>



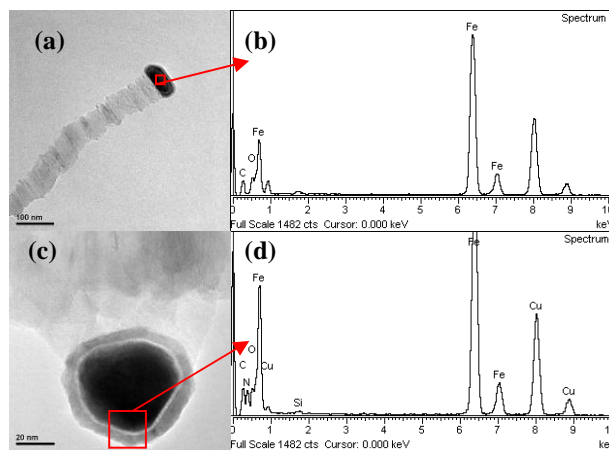
**Figure 3.** Effect of reaction temperature on  $\text{NH}_3$  conversion (0.4g catalyst; GHSV,  $6500 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ).



**Figure 4.** Conversion as a function of time for  $\text{NH}_3$  decomposition over Fe-mica/CNFs (0.4 g catalyst; reaction temperature,  $550 \text{ }^\circ\text{C}$ ; GHSV,  $6500 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ).

With the mica support, Fe particles are smaller, more uniform, and have more accessible surface, which accounts for the higher activity of the catalyst (Figure 3). An almost complete conversion of  $\text{NH}_3$  over Fe-mica/CNFs could be achieved at  $620 \text{ }^\circ\text{C}$  at a space

velocity of  $6500 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . Also the Fe-mica/CNFs has a good stability (Figure 4), which is because of the physical isolation of the Fe particles by the CNFs and mica.



**Figure 5.** HRTEM-EDS images of Fe nanoparticles on mica/CNFs composite before (a and b) and after (c and d) reaction.

As evidenced in Figure 5,  $\text{FeN}_x$  is the primary active phase in Fe-mica/CNFs, and Fe/C core-shell and Fe- $\text{FeN}_x$ /C core-shell structures were directly observed by HRTEM and EDS. The carbon layer on the Fe particle was found before and after  $\text{NH}_3$  decomposition, which is formed by precipitation of the dissolved carbon in the Fe particle. The carbon layer will dissolve again into Fe at high temperature, leaving exposed uncovered surface for  $\text{NH}_3$  decomposition. This explains the activation period observed in Figure 4. The presence of the iron nitride phase in such catalysts provides hints on the mechanism and helps to establish the microkinetics of the reaction.

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