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## Support-Induced Oxidation State of Catalytic Ru Nanoparticles on Carbon Nanofibers that were Doped with Heteroatoms (O, N) for the Decomposition of NH<sub>3</sub>

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Ru nanoparticles were supported on monoliths that were coated with variously functionalized carbon nanofibers (CNFs), that is, un-doped CNFs, CNFs that had been post-treated with  $H_2O_2$ , and CNFs that had been doped with nitrogen during their growth. The Ru uptake (by equilibrium adsorption) onto N-doped CNFs was larger compared to that on their un-doped and O-doped counterparts. The functionalization of the CNF support did not play a significant role in determining the size

#### Introduction

Carbon nanofibers (CNFs) or carbon nanotubes (CNTs) that are doped with nitrogen have shown superior performance to their un-doped counterparts as catalyst supports for different reactions. For instance, they have been used to support Ru catalysts for ammonia decomposition,<sup>[1,2]</sup> to support Pt electrocatalysts<sup>[3]</sup> or Fe catalysts<sup>[4]</sup> for the oxygen-reduction reaction, as Pd supports for the direct synthesis of  $H_2O_2$  from  $H_2$  and  $O_{2'}^{[5]}$ as Pd supports for the hydrogenation of cynamaldehyde,<sup>[6]</sup> as supports of Pd and Au for the selective aerobic oxidation of alcohols,<sup>[7]</sup> and as supports of Au for the preferential oxidation of CO.<sup>[8]</sup> There are several benefits to N-doped carbon supports, such as improved activity, owing to better dispersion of the catalyst,<sup>[1,7]</sup> increased selectivity,<sup>[6,9]</sup> owing to specific interactions between the doped support and the metal, and enhanced stability, because the nitrogen groups contribute to keeping the metal particles well-dispersed<sup>[8, 10]</sup> and in a reduced state.<sup>[11,12]</sup> This enhanced performance could be attributed to either geometric effects, because the doping can govern the size and structure of the metal nanoparticles, or to electronic effects on the metal nanoparticles, owing to the high electronic conductivity of the graphitic carbon atoms.

 $\rm NH_3$  has been put forward as a very promising  $\rm H_2$ -storage media for small-scale fuel cells in some niche applications.<sup>[13]</sup> Ammonia has high gravimetric (17.7 wt.%) and volumetric  $\rm H_2$  capacities, the latter of which is about 45% larger than that of liquid hydrogen. It poses no danger of explosion and it can be easily stored as a liquid at room temperature and at 8.6 bar,

of the deposited Ru nanoparticles, but it substantially impacted on the sintering under the reaction conditions and on the electron density of the reduced metal. Among the catalysts on the different CNF supports, Ru on N-CNF exhibited the highest  $H_2$  productivity from ammonia decomposition, which pointed to electronic effects that were induced by functionalization of the support.

whereas  $H_2$  requires very low temperatures (20 K) and expensive tanks to adopt its liquid form. Alternative ammonia sources, both in the liquid and solid states, have also been proposed to generate  $H_2$ , such as  $urea^{[14]}$  or metal ammines.<sup>[15]</sup> Thus, the safety issues with regards to its storage and handling are well-established.<sup>[15,16]</sup> More importantly, the product stream (hydrogen/nitrogen) is CO-free and the amount of unconverted ammonia can be decreased to less than 200 ppb by using a suitable adsorbent. Therefore, the  $H_2$  stream can be fed directly into a fuel cell without further purification steps, which are needed for  $H_2$  that is generated from hydrocarbon reforming. The decomposition of NH<sub>3</sub> is a key step in the implementation of this technology. Therefore, it is necessary to develop robust catalysts that are active at low temperatures.

To shed some light on the effect of the N doping of a CNF support on the metal catalyst and its catalytic performance in ammonia decomposition, herein, we have used un-doped CNFs and CNFs that were doped with two heteroatoms (O, N) as a Ru support. Doping with O and N atoms was either performed by postfunctionalization with  $H_2O_2$  or by in situ doping during CNF growth, respectively. The catalysts were characterized by STEM, XPS, and TPR. CNF functionalization did not significantly affect the Ru-particle size. On the contrary, the oxidation state of the impregnated fresh catalyst and the electronic charge on the reduced Ru catalyst markedly depended on the doping of the CNF support. The characterization results can explain the higher  $H_2$  productivity with the N-CNF-supported catalyst.

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#### **Experimental Section**

# Growth of un-doped CNFs and N-doped CNFs on cordierite monoliths

The CNFs and N-CNFs were grown on cordierite monoliths according to literature procedures.<sup>[17,18]</sup> Cordierite monoliths (diameter: 1 cm, length: 5 cm, 400 cpsi; Corning) were wash-coated with alumina by using a dip-coating method that was similar to the sol-gel coating method described by Nijhuis et al.<sup>[19]</sup> In this method, a sol was prepared from pseudoboehmite (AlOOH, Pural; Sasol), urea, and a 0.3 M aqueous solution of nitric acid with a weight ratio of 2:1:5. After stirring for 30 min, the dried monolith was dipped in the sol. The liquid inside the monolith channels was removed by thoroughly flushing with pressurized air and then drying at RT for 24 h, with continuous rotation around its axis. Finally, the monolith was calcined in air at a rate of 1 K min<sup>-1</sup> up to 873 K to obtain the  $\gamma$ -alumina wash-coating.

Nickel was deposited by adsorption from a pH-neutral solution according to a literature procedure.<sup>[20]</sup> Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (29 g; Sigma–Aldrich), NH<sub>4</sub>NO<sub>3</sub> (80 g; Sigma–Aldrich), and ammonia solution (25%, 4 mL) were mixed in a 1 liter bottle. The monolith samples were kept overnight in this solution under a continuous flow of the liquid through their channels. Then, the monoliths were rinsed thoroughly with deionized water, followed by drying first at RT overnight and then at 373 for 1 h. Subsequently, the monoliths were calcined in a flow of nitrogen gas (1 Kmin<sup>-1</sup>) up to 873 K, followed by a dwell time of 2 h. The Ni content in the monoliths was measured by inductive coupled plasma-optical emission spectroscopy (ICP-OES).

For the growth of the CNFs and N-CNFs, the monoliths were fitted in a quartz reactor by wrapping in a quartz band. The reduction of the calcined catalyst was performed under a hydrogen atmosphere at 823 K for 120 min (5 Kmin<sup>-1</sup>). Then, the monolith was heated (5 Kmin<sup>-1</sup>) to 873 K. Once this temperature had been reached, a gaseous mixture of  $C_2H_6/H_2$  (50:50) or  $C_2H_6/NH_3$  (50:50, 100 mLmin<sup>-1</sup>, standard temperature and pressure) was fed into the reactor for the growth of samples, which were denoted as CNFs and N-CNF, respectively. The growth of the CNFs was allowed to proceed for 2 h, following up by cooling under an inert atmosphere. This reaction time was long enough for the catalyst to be deactivated, as corroborated by gas chromatography analysis of the flue gas.

The CNF-monolith was also subjected to oxidation treatment with  $H_2O_2$  at RT for 20 h. During this treatment,  $H_2O_2$  was continuously flowed through the channels of the monolith. This sample was denoted as O-CNF.

# Adsorption of the Ru precursor onto the CNF-based supports

For the adsorption of the metal-nanoparticle precursor onto the CNF-, O-CNF-, and N-CNF-coated monoliths, an equilibrium-adsorption method was used. First, an aqueous solution of Ru nytrosil nitrate ([Ru(NO)(NO<sub>3</sub>)], 40 mL) was prepared. The amount of metal that was added into the solution was calculated to be 5 wt.% with respect to the weight of the CNFs, which led to a ruthenium concentration of 500–700 ppm in the solution. The CNF-, N-CNF-, and O-CNF-coated monoliths were introduced into a tube with the metal solution and the vial was continuously rotated overnight perpendicular to the axial direction. This procedure guaranteed the continuous flow of the liquid through the channels of the monolith and the homogenization of the solution. After this step, a small

piece of the monolith (0.5 cm) was cut off and characterized. This sample was denoted by the name of the support followed by "fresh". The metal uptake was calculated from the analysis of the initial and final solutions by inductive coupled plasma-optical spectrometry (ICP-OES).

Subsequently, the monolith was rinsed with copious amounts of water, dried at 380 K, calcined under a  $N_2$  atmosphere, and reduced in a flow of  $H_2$  at 473 K by using a heating rate of 1 Kmin<sup>-1</sup>. The sample after this calcination and reduction treatment was denoted by the name of the support followed by "reduced".

#### Characterization

Ex situ XPS spectra were recorded on an ESCAPlus Omnicrom system that was equipped with an Al<sub>Ka</sub> radiation source to excite the sample. Calibration of the instrument was performed with the Ag 3d<sub>5/2</sub> line at 368.27 eV. All of the measurements were performed under ultrahigh vacuum (UHV, < 10<sup>-10</sup> Torr). Internal referencing of the spectrometer energies was performed by using the dominant C 1s peak of the support at 284.6 eV and the Al 2p peak at 74.3 eV. The program that was used to perform the curve-fitting of the spectra was CasaXPS after performing a baseline Shirley method. Because the binding energy of Ru 3d overlapped with the C 1s region (284.6), we used the Ru 3p<sub>3/2</sub> region (458–468 eV) to determine the atomic content of ruthenium species in the catalyst. The analysis of the Ru XPS peak enabled the determination of Ru<sup>o</sup>, Ru<sup>4+</sup>, and Ru hydrate at 461.2–461.6, 463.4–463.8, and 465.7–466.1 eV, respectively.<sup>[21,22]</sup>

In situ XPS was also performed. To this end, prior to recording the XPS spectra, the passivated catalyst was reduced in situ with a flow of  $H_2$  at 473 K. Therefore, the reduced sample was not exposed to air before the XPS measurements, thereby avoiding re-oxidation.

The size of the Ru nanoparticles on the carbon nanofibers was studied by using scanning transmission electron microscopy (STEM) on a FEI TECNAI F30 electron microscope that was equipped with a Gatan Energy Filter and a cold-field emission gun (FEG) operating at 300 kV with a lattice resolution of 1.5 Å. TEM specimens were prepared by ultrasonically dispersing the powder that was retrieved from the monoliths in EtOH. A drop of the suspension was applied to a holey carbon support grid. The particle-size distribution was calculated by statistical analysis of 300 particles on the CNF from about 20 images.

Temperature-programmed reduction (TPR) profiles were measured on a Micromeritics PulseChemisorb 2700. After placing the sample in the holder and flowing a mixture of 10% H<sub>2</sub> in Ar, the temperature was increased from 313 to 573 K at a rate of 5 K min<sup>-1</sup>.

#### **Catalytic testing**

To compare the intrinsic activity of the catalysts for  $NH_3$  decomposition, the monoliths were crushed into powders with particle size < 100 µm. The powdered catalyst (200 mg) was diluted with SiC and placed between quartz wool in the middle of a reactor tube (6 mm i.d.). Subsequently, the reactor was placed in the constant-temperature zone of a furnace that was equipped with a temperature controller (Eurotherm). The flow rate of the feed gas (5% anhydrous ammonia in Ar) that was used for the catalyst testing was fixed at 33 mLmin<sup>-1</sup> by using Bronkhorst mass-flow controllers. The reactant dilution minimized the increase in volume at high conversion. The absence of diffusional limitations was assessed by applying the Weisz–Prater criterion.<sup>[23]</sup> The absence of external diffusion limitations was corroborated because increasing the flow rate did not lead to a further increase in activity.

The passivated catalysts were in-situ reduced at 473 K and subsequently tested in the decomposition of  $NH_3$  at temperatures between 573–773 K. First, the conversion was measured at the highest temperature until it stabilized. Then, the temperature was decreased in 50 K steps and the conversion measured until it stabilized. Subsequently, the conversion was also measured by stepwise increasing the temperature to check the repeatability of the experiment. The outlet gases were analyzed on an Agilent Micro GC 3000A;  $H_2$  and  $N_2$  were analyzed by using a molsieve column and  $NH_3$  was analyzed by using a Plot-Q column.

#### **Results and Discussion**

The size of the Ru particles on the supports was characterized by using STEM. On all of the supports, the particle-size distribution (Figure 1) was very narrow and all of the Ru particles were very small, with average sizes of  $(1.42\pm0.022)$ ,  $(0.95\pm0.017)$ ,  $(1.28\pm0.018)$  nm for Ru on CNF, O-CNF, and N-CNF, respectively.

Table 1 shows the metal uptake of Ru on the CNFs with different surface chemistry. The metal uptake was 25% larger on N-CNFs than on un-doped CNFs and O-CNF. In a previous report,<sup>[24]</sup> we observed that the amount of pyridinic groups on N-CNF decreased after metal deposition, thus suggesting that these groups could play a role in the adsorption of the metal precursor. This result was in agreement with other reports,<sup>[1]</sup> which showed that the pyridinic groups interacted strongly with Ru<sup>3+</sup>. They found that the average size of the Ru particles decreased with increasing content of pyridinic nitrogen atoms. In contrast, we did not observe any significant effect of nitrogen groups on the Ru-particle size.

To study the reduction state of the metal at the different preparation stages, the catalysts were characterized by ex situ XPS (Figure 2) and TPR (Figure 3) upon impregnation of the metal precursor (fresh) and after reduction and exposure to air (reduced). Quantitative XPS analysis of the reduced catalysts revealed that the O/C ratios (at.%) were 16:1, 24:1, and 7.2:1 for the CNF-, O-CNF-, and N-CNF-supported catalysts, respectively. After the reaction, the O/C ratios decreased slightly to 13:1, 17:1, and 6.5:1, respectively. The XPS N/C ratio (at.%) of the reduced N-CNF catalyst was 5.2:1. The N/C ratio remained unchanged (within experimental error) after reduction and after the reaction (see the Supporting Information). The proportion of each type of nitrogen species changed after the re-



Figure 1. Representative STEM images and particle-size distributions of reduced Ru catalysts that were supported on a) un-doped CNF, b) O-CNF, and c) N-doped CNF. Scale bars = 20 nm.

action, with the peak for the pyridine oxide species disappearing, whereas the amount of pyridinic and pyrrolic nitrogen species increased.

The quantitative results of Ru XPS peak deconvolution are also listed in Table 1. Upon impregnation of Ru onto the supports, the percentage of metallic catalyst, that is, the percentage of Ru in its zero oxidation state (Figure 2 and Table 1), was

Sample	Ru uptake	XPS peak position			TPR		
	per CNF [wt.%]	[e Ru <sup>o</sup>	V] (abundance [% RuO <sub>2</sub>	) RuO <sub>2</sub> •H <sub>2</sub> O	Peak maximum [K]	H <sub>2</sub> consumed [cm <sup>3</sup> g <sup>-1</sup> Ru]	Abundance of oxidized Ru <sup>[a]</sup> [%
Ru/CNF fresh	3.9	461.0 (0)	463.8 (46)	466.0 (54)	416.8	2323	100
Ru/O-CNF fresh	3.7	461.8 (9)	464.3 (57)	466.0 (34)	405.0	1260	100
Ru/N-CNF fresh	5.1	462.6 (18)	464.0 (64)	465.8 (18)	407.6	2333	100
Ru/CNF reduced	3.9	461.8 (43)	463.4 (38)	465.7 (19)	353	1323	56.9
Ru/O-CNF reduced	3.7	461.8 (19)	463.4 (53)	465.4 (28)	348	782	62.0
Ru/N-CNF reduced	5.1	461.8 (54)	463.4 (34)	465.4 (12)	338	226	9.7

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**Figure 2.** XPS Ru  $3p_{3/2}$  spectra of the metal catalysts that were adsorbed onto un-doped CNF, N-doped CNF, and O-CNF after two (ex situ) preparation stages, that is, just after impregnating the precursor (fresh) and after reduction at 473 K and exposure to air at room temperature (reduced).



**Figure 3.** TPR profile of the Ru catalysts that were adsorbed onto un-doped CNF, N-doped CNF, and O-CNF after two preparation stages, that is, just after impregnating the precursor (fresh) and after reduction at 473 K and exposure to air at room temperature (reduced).

about 18% on N-doped CNFs, whereas it was significantly lower or zero on the other functionalized CNFs. This result suggests that nitrogen groups cooperate to reduce the Ru<sup>2+</sup> precursor upon impregnation and, hence, fixing it onto the support. This process can account for the higher metal loadings on N-CNF and guarantees that the catalyst precursor is uniformly distributed along the N-CNF monolith, as observed by TEM at different monolith locations.

The impregnated catalyst that was prepared as described above was reduced at 473 K in a flow of  $H_2$ . TPR measurements of the fresh catalysts (Figure 3) demonstrated that this temperature was high enough to reduce the Ru precursor. However, if the reduced catalysts were subsequently exposed to air, part of metal was re-oxidized, as evidenced by a small low-temperature reduction peak in the TPR spectrum of the reduced catalyst between 338-353 K. Both ex situ XPS and TPR techniques revealed that the extent of re-oxidation was lower if supported on N-doped CNFs compared to its un-doped and oxidized counterparts. This result was corroborated by integration of the TPR peaks of the reduced catalyst (Table 1), which showed that 90% Ru was in its metallic state for Ru on N-doped CNF, whereas only 43% and 38% of Ru was metallic if supported on un-doped and oxidized CNFs, respectively. From the XPS deconvolution, 54%, 43%, and 19% of Ru was metallic Ru on N-doped, un-doped, and oxidized CNFs, respectively. The differences between these percentages of the reduced metal as measured by XPS were smaller than those measured by TPR. The degree of re-oxidation as measured by XPS was generally larger than that measured by TPR, thus indicating that the reoxidation mainly occurred at the catalyst surface. Both techniques confirmed that the degree of re-oxidation of the two metals upon exposure to air followed the order: N-CNF ≪ CNF < O-CNF. Therefore, nitrogen groups contributed to keeping the metal in its reduced state on exposure to an O<sub>2</sub> atmosphere, which could be attributed to the electron-donating properties of nitrogen on highly conducting graphitic structures.<sup>[25]</sup> Clearly, under the reaction conditions (reducing atmosphere, high temperature), the metal must be in its reduced state. The extent of re-oxidation at room temperature is considered herein as a descriptor of electron donation from supports with different types of functionalization. Operando spectroscopic techniques are planned to confirm the electron donation from the support under these reaction conditions.

Besides ex situ XPS characterization, in situ XPS characterization of Ru/CNF and Ru/N-CNF was also performed (Figure 4). During this characterization process, the catalyst was reduced in the XPS chamber at 473 K and XPS spectra were recorded without exposing the sample to the atmosphere. Only one peak, which corresponded to reduced Ru, was observed for both catalysts. The center of the peak was shifted by 0.3 eV for Ru supported on CNF compared to that on N-CNF, which indi-



Figure 4. XPS Ru  $3p_{\rm 3/2}$  spectra of Ru/N-CNF and Ru/CNF that were reduced in situ at 473 K.

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cated that the electronic density on the ruthenium was slightly larger if supported on N-CNF for the fully reduced catalyst.

These Ru catalysts were tested in the decomposition of  $NH_3$  for in situ  $H_2$  generation. A plot of conversion versus temperature is shown in Figure 5. Ru supported on N-CNF (Ru/N-CNF) showed significantly higher conversion than Ru on the other



**Figure 5.** Plot of NH<sub>3</sub> conversion as a function of temperature in the steady state (after an initial stabilization period) for the different catalysts: Ru/CNF ( $\blacktriangle$ ), Ru/O-CNF ( $\blacksquare$ ), and Ru/N-CNF ( $\bigcirc$ ); dashed line denotes the N-CNF support. Inset shows the NH<sub>3</sub> conversions over 72 h at 723 K.

supports at the same temperature. On approaching complete conversion, the differences in conversion between the catalysts became less apparent, because the reaction rate has been reported to be proportional to the concentration of  $NH_3$  and inhibited by the  $H_2$  product.<sup>[26]</sup> At  $NH_3$  conversions close to 100%, the influence of the concentrations of the reactants and products prevailed over the intrinsic catalyst activity.

Because the Ru loading in Ru/N-CNF was larger than in the other samples, the specific  $H_2$  productivity (per mg of Ru) at 723 K was calculated to enable a comparison between all of the catalysts (Table 2). Normalized to the amount of Ru catalyst, the Ru/N-CNF catalyst still exhibited higher  $H_2$  productivity, which could be attributed to the higher intrinsic activity of the catalyst that was supported on N-CNF compared to those supported on CNF with other types of functionalization.

The inset in Figure 5 shows the  $NH_3$  conversion at 723 K over 72 h for the different catalysts. The conversion decreased at the start of experiment and then remained stable (within ex-

perimental error). Statistical analysis of the STEM images of the catalysts after the reaction (see the Supporting Information) revealed an average Ru size of  $(1.35\pm0.020)$ ,  $(1.47\pm0.027)$ , and  $(1.19\pm0.023)$  nm for Ru on CNF, O-CNF, and N-CNF, respectively. Compared with the Ru mean size of the reduced catalysts before the reaction (Figure 1), the Ru particle sizes did not increase after the reaction, except for the catalyst that was supported on O-CNF, which underwent a 50% increase in particle size. The initial decrease in activity could be explained by initial restructuring of the metal catalyst or support on exposure to the reaction conditions.

To gain insight into the interactions between the metal particles on the N-doped carbon support, a survey of the literature regarding the interactions of metal nanoparticles with undoped carbon materials was performed. The interactions of metal particles with un-doped carbon materials has been welldescribed elsewhere.<sup>[27]</sup> For un-doped activated carbon materials, unsaturated surface carbon atoms on the edges or defects of graphite planes have been found to form very strong bonds with metal atoms.<sup>[28]</sup> At very low loadings, that is, small nanoparticles, molecular-orbital analysis indicated that metal atoms on activated carbon surface were positively charged, owing to the extremely effective delocalized donor-acceptor interactions with the  $\pi$  system of the support. Increasing the loading, that is, employing larger nanoparticles, caused a decrease in the corresponding net charge. The positive charge on Pd agreed with the highest Pd 3d binding energies for the Pd cluster on graphite with a mean diameter of less than 1 nm relative to the bulk metal.<sup>[29]</sup> Larger Pd clusters (> 5 nm) showed binding energies that were close to the value of the bulk metal (335.1 eV). The shift in the binding energy relative to the bulk metal was as large as +1.2 eV in clusters of diameter <1 nm. According to the literature reports mentioned above, smaller metal particles on un-doped carbon materials gave rise to higher binding energies, owing to electron transfer from the metal to the support. Comparing the binding energies of the metals on the different CNF-based supports that were prepared herein, the smallest positive charge on the metal atoms on N-CNFs could not be explained by metal-particle-size effects because STEM analysis showed that the metal particles were very similar and there were no particles larger than 2.5 nm for all of the catalysts. Thus, the difference in the oxidation state of Ru on the different CNF supports should be attributed to the effect of electronic donation of the support rather than to particle-size effects.

Recently, Chen et al. also reported that Pd metal was in a more-reduced state on N-CNT than on O-CNT for both the fresh and reduced catalysts.<sup>[30]</sup> In addition, they observed

Table 2. Catalytic activity for $H_2$ production from the catalytic decomposition of $NH_3$ .								
	weight of CNF	weight of monolith	at 723 K	at 723 K				
	[wt.%]	[wt.%]	[%]	[mmol mgRu <sup>-1</sup> h <sup>-1</sup> ]				
Ru/CNF reduced	3.9	0.267	72.1	8.95				
Ru/O-CNF reduced	3.7	0.253	69.3	9.08				
Ru/N-CNF reduced	5.1	0.309	86.4	9.27				

smaller Pd particle size for the N-CNT-supported catalyst at similar metal loadings. Herein, Ru showed a larger metal loading on N-CNF than on CNF and O-CNF, which may also affect the metal-particle size. Despite its higher metal loading, after the reaction, Ru on N-CNF had suf-

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fered less sintering than Ru on O-CNF. Thus, although the Ruparticle size was smaller on O-CNF for the reduced catalyst before the reaction, after the reaction, the smallest metal-particle size corresponded to the catalyst on N-CNF.

#### Conclusions

Monoliths that were coated with variously functionalized carbon nanofibers, that is, un-doped CNFs, CNFs that had been post-treated with H<sub>2</sub>O<sub>2</sub>, and CNFs that were doped with nitrogen during the growth process, have been used as supports for Ru catalysts. After impregnating a ruthenium-nitrate precursor onto the different supports by equilibrium adsorption, the fresh and reduced catalyst were characterized by STEM, TPR, and ex situ and in situ XPS. XPS characterization of the fresh catalyst showed that the ruthenium-nitrate precursors had become partially reduced (ca.18%) upon impregnation onto N-doped CNF, whereas the extent of metal reduction upon impregnation on un-doped or O-doped CNFs was significantly lower. This support-mediated metal reduction could account for the larger metal uptake on N-doped CNFs compared to the other supports. Likewise, N-doped CNFs adsorbed 25% more Ru metal than un-doped and O-doped CNFs. Moreover, XPS characterization demonstrated that electron donation from the support to the metal was larger for N-doped CNFs compared to the un-doped and O-doped CNFs. Very small particle sizes (mean size: 1 nm) and narrow particle-size distribution were found for all of the supports, regardless of the type of functionalization. After the reaction, Ru on O-CNF suffered more sintering than Ru on CNF or N-CNF. Ru that was supported on N-CNF induced significantly higher conversion in the decomposition of NH3 than that on the other supports. The catalysts were stable for (at least) 72 h reaction time at 723 K. Therefore, Ru/N-CNF is an excellent candidate catalyst for H<sub>2</sub> generation from NH<sub>3</sub> to feed fuel cells. Furthermore, its monolithic shape endows it with robustness and portability.

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**Keywords:** doping • heterogeneous catalysis • nanostructures • ruthenium • supported catalysts

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