# Ruthenium Clusters on Carbon Nanofibers for Formic Acid Decomposition: Effect of Doping the Support with Nitrogen

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The catalytic properties of 1 wt% Ru catalysts with the same mean Ru cluster size of 1.4–1.5 nm supported on herringbone-type carbon nanofibers with different N contents were compared for H<sub>2</sub> production from formic acid decomposition. The Ru catalyst on the support with 6.8 wt% N gave a 1.5–2 times higher activity for the dehydrogenation reaction (CO<sub>2</sub>, H<sub>2</sub>) than the catalyst on the undoped support. The activity in the dehydration reaction (CO, H<sub>2</sub>O) was the same. As a result, the selec-

# Introduction

Formic acid can be produced from renewable biomass as a byproduct of the acid-catalyzed hydrolysis of cellulose to levulinic acid.<sup>[1]</sup> It can also be produced as a primary product of the oxidation of cellulose with oxygen using heteropoly acids and their salts as catalysts.<sup>[2]</sup> As formic acid contains a sufficient amount of hydrogen (4.4 wt%), it is considered as a potential source of hydrogen for applications in fuel cells<sup>[3]</sup> or as a hydrogen donor for some hydrogenation reactions instead of molec-

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tivity to  $H_2$  increased significantly from 83 to 92% with Ndoping, and the activation energies for both reactions were close (55–58 kJ mol<sup>-1</sup>). The improvement could be explained by the presence of Ru clusters stabilized by pyridinic N located on the open edges of the external surface of the carbon nanofibers. This N may activate formic acid by the formation of an adduct (>NH<sup>+</sup>HCOO<sup>-</sup>) followed by its dehydrogenation on the adjacent Ru clusters.

ular hydrogen.<sup>[1b,4]</sup> Therefore, it is important to develop effective catalysts to direct the decomposition of formic acid towards dehydrogenation to give  $H_2$  and  $CO_2$  as products, rather than in the direction of dehydration to give  $H_2O$  and CO, as CO is a catalyst poison.

Often, a variety of carbon materials are used as catalyst supports for noble metals that decompose formic acid under mild conditions. Such supports attract attention as inert and highsurface-area materials able to stabilize metals in a highly dispersed state. Carbon nanofibers (CNFs) have attracted much interest because of their exceptional structural and textural properties and there is a possibility to control their properties during synthesis.<sup>[5]</sup> Modification of the composition of CNFs opens up new routes to improve the performance of a catalyst.<sup>[5c,6]</sup> Recently, we showed that the doping of CNFs supports with N led to an increase of the formic acid decomposition activity of Pt catalysts by a factor of 10 if Pt is dispersed as 1 nm clusters.<sup>[7]</sup> However, Pt is a very expensive metal, and cheaper metallic catalysts are highly desirable. Ru can be considered as such a substitute for Pt as it has demonstrated catalytic properties for formic acid decomposition comparable to that of Pt.<sup>[8]</sup> We have also shown that Ru catalysts on N-doped CNFs provide an improved activity and stability during the wet-air oxidation of phenol compared to Ru catalysts on undoped CNFs.<sup>[9]</sup> Moreover, Marco et al.<sup>[6b]</sup> discovered that Ru supported on N-doped CNFs showed improved properties for the decomposition of ammonia. Generally, the N-doping of carbons is useful to create improved materials for a wide range of applications.<sup>[6a, 10]</sup>

In contrast to Pt/C catalysts, Ru/C catalysts are applied widely in reactions related to biomass conversion, especially hydrogenation, that could use hydrogen donor molecules such

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as formic acid or alcohols. Thus, Panagiotopoulou and Vlachos<sup>[11]</sup> showed high yields of methylfuran from hemicellulosederived furfural over a Ru/C catalyst at  $\approx\!453\,$  K. In this case, methylfuran was produced by the transfer hydrogenation reaction using 2-propanol. Earlier, West et al.<sup>[12]</sup> applied Ru/C catalysts for the hydrogenation of biomass-derived ketones and acids to alcohols. The same group<sup>[1b]</sup> reported that the use of Ru/C catalysts can be promising for the conversion of levulinic acid to  $\gamma$ -valerolactone by transfer hydrogenation with formic acid. Similarly, Heeres et al.<sup>[4b]</sup> produced  $\gamma$ -valerolactone from C<sub>6</sub> sugars by dehydration/transfer hydrogenation with formic acid on Ru/C catalysts. Notably, methylfuran, y-valerolactone, and alcohols can be used as motor fuel additives or as valuable chemical intermediates. For efficient transfer hydrogenation with formic acid, metal-based catalysts should facilitate the decomposition of formic acid to give hydrogen at low temperatures.

Although transfer hydrogenation with formic acid looks promising for a wide set of reactions, the decomposition of formic acid over Ru/C catalysts has been studied to a much lesser extent than that over Pd, Pt, Au, and Ni catalysts. Solymosi et al.<sup>[13]</sup> showed that the activity of a Ru/C catalyst was higher than that of a Rh/C catalyst but lower than the activities of Ir, Pt, and Pd catalysts supported on carbon. O'Neill et al.<sup>[14]</sup> studied the decomposition of formic acid in the liquid phase in the presence of water and showed that the activity of a Ru/C catalyst was lower than that of a Pd/C catalyst. Unfortunately, all these comparisons were performed for catalysts with different metal dispersions.

In the present study, formic acid decomposition was investigated over 1 wt % Ru catalysts supported on CNFs doped with different amounts of N. The advantage of these catalysts was that the Ru clusters formed possessed approximately the same mean size of  $\approx$  1.4–1.5 nm on undoped and N-doped supports. The size of the metal particles may decrease for the N-doped carbon supports compared to that on the undoped supports.<sup>[10,15]</sup> This can complicate the understanding of the real reasons for the N-doping effect, as structure-sensitivity effects related to the metal particles size can mask it. In the present paper, we show clearly that the selectivity to hydrogen increased noticeably with the amount of N in the support. This was achieved by an increase in the rate of dehydrogenation, whereas the dehydration rate did not change. Additionally, certain differences were observed for the state of the Ru clusters in the N-doped samples as compared to the undoped samples, which arise from the participation of the support N sites in the coordination of these clusters.

## **Results and Discussion**

Characterization of the Ru/N-CNFs samples

## Characterization of the supports by N<sub>2</sub> adsorption

The BET surface areas for the N-CNFs supports with 0, 2, and 6.8 wt% N were 229, 303, and  $209 \text{ m}^2 \text{g}^{-1}$ , respectively (Table S1). The average pore diameters were in the range of 8.2–11.7 nm, and the pore volumes were in the range of 0.47–

 $0.88 \text{ cm}^3 \text{g}^{-1}$ . The contribution of micropores to the total pore volume was negligibly small (<2%). These data indicate that all the N-CNFs supports were mesoporous materials. The textural characteristics of the materials almost did not change after the Ru deposition.

### **TEM characterization**

TEM was used to determine the mean Ru particle size and particle size distributions for the Ru catalysts, and typical images of the catalysts are shown in Figure 1. The catalyst support used displays approximately the same diameter of carbon nanofibers of  $\approx$  30 nm. The morphology of the fibers allows their assignment as a herringbone-type structure that contains a lot of open edge sites of the graphene layers.<sup>[5b,c]</sup> The distributions of Ru particle sizes obtained for the catalysts with 0, 2, and 6.8 wt% N are monomodal and narrow with mean particle sizes of 1.4, 1.4, and 1.5 nm with almost the same standard deviations of 0.3, 0.2, and 0.2 nm, respectively (Table 1). The mean Ru particle sizes correspond to 88–94% dispersion,



Figure 1. TEM images of the Ru/N-CNFs catalysts and Ru particle size distributions.



Table 1. N and Ru contents in the samples, mean Ru particle sizes determined by TEM, TOF for the total formic acid decomposition, and apparent activa- tion energies ( <i>E<sub>a</sub></i> ) for the dehydration and dehydrogenation reactions.								
Catalysts	N [wt%]	Ru [wt%]	Mean Ru particle size [nm]	TOF at 373 K [s <sup>-1</sup> ]	$E_{\rm a}$ for dehydration [kJ mol <sup>-1</sup> ]	$E_a$ for dehydrogenation [kJ mol <sup>-1</sup> ]		
1.3Ru/0N-CNFs	0	1.3	1.4±0.3	0.009	57	55		
1.3Ru/2N-CNFs 1Ru/6.8N-CNFs	2 6.8	1.3 1.0	$1.4 \pm 0.2$ $1.5 \pm 0.2$	0.011	56 56	58		

which implies that almost all the Ru in the particles on the studied supports was available for the catalytic reaction.

#### Photoelectron spectroscopy

Photoelectron spectroscopy was used to analyze the chemical states of N and Ru in the samples. Apart from the collection of the spectra for the original samples, the spectra of the 1Ru/ 6.8N-CNFs catalyst reduced in  $H_2$  at 623 K in the preparation chamber of the spectrometer were used to clarify the Ru states. N 1s spectra (Figure 2) of the 1.3Ru/2N-CNFs, 1Ru/6.8N-CNFs, and 1Ru/6.8-CNFs catalysts after reduction were fitted



Figure 2. N 1s spectra of 1.3Ru/2N-CNFs (1), 1Ru/6.8N-CNFs (2), and 1Ru/ 6.8N-CNFs (3) after reduction.

with four peaks with intensity maxima at binding energies of 398.6, 399.8–400.0, 400.7–400.9, and 402.0 eV that can be assigned to pyridinic, pyrrolic, graphite-like (quaternary), and oxidized N species, respectively.<sup>[10,16]</sup> The intensity of the pyridinic N relative to the total intensity of the N1s spectrum was 27 and 37% for the 1.3Ru/2N-CNFs and 1Ru/6.8N-CNFs samples,

respectively. The contribution of this peak to the overall N1s spectrum became stronger after reduction (45%). The impact of the pyrrolic N peak decreased from 37 to 26% with the increase of N content from 2 to 6.8 wt%. The relative content of the graphite-like (quaternary) N was in the range of 27–29% for all samples. The contribution of the oxidized N species decreased slightly from 8 to 5% after reduction.



**Figure 3.** Ru 3d<sub>5/2</sub> spectra of a) 1.3Ru/ON-CNFs (1) and 1.3Ru/2N-CNFs (2); b) 1Ru/6.8N-CNFs (1) before and (2) after reduction (the spectra were recorded at  $h\nu = 600$  eV).



The Ru3d<sub>5/2</sub> spectra for all samples are shown in Figure 3. Following the spectral fitting, two peaks are observed at binding energies of 280.6-280.9 and 281.2-281.4 eV (Figure 3 a and b curve (1)). According to the literature data, the latter peak can be assigned to an oxidized Ru species similar to that in  $RuO_2$ .<sup>[17]</sup> The  $Ru3d_{5/2}$  binding energy value obtained for the former component is higher than the value typical for the bulk metallic state of Ru (~280.0 eV).<sup>[9,17a,18]</sup> It is well known that the size of particles and their shape can influence the binding energy because of the initial and final state effects.<sup>[19]</sup> A positive shift in the binding energy can be the result of the charging of Ru clusters through their interaction with the support or the adsorption of some carbon- or oxygen-containing species on their surface. Thus, we can assign the peak at a binding energy of 280.6-280.9 eV to very small metallic Ru<sup>0</sup> clusters or to a slightly charged species  $Ru^{\delta+}$ .

It is interesting that the highest content of these reduced Ru species was observed for the sample with the maximum N content (6.8 wt%). The ratio of the intensities of these species to the oxidized species increased by  $\approx$  1.5 times as compared to that of the undoped sample. A similar result was obtained by Marco et al.<sup>[6b, 20]</sup> for samples with a higher concentration of Ru (3.5–5 wt%). These authors also observed an increase in the content of metallic Ru species with the introduction of N into the CNFs. We propose that the N-doped support facilitates the formation of Ru with a higher contribution of the metallic clusters or slightly charged Ru<sup>δ+</sup> species in agreement with the literature data that reports the stabilization of Ru particles in a reduced state through electron donation from the N-modified carbon support.<sup>[20]</sup>

The additional treatment of 1Ru/6.8N-CNFs with hydrogen results in the complete reduction of the oxidized Ru species. Only one peak was observed in the Ru  $3d_{5/2}$  spectrum (Figure 3 b curve (2)) at a binding energy of 280.3 eV close to the peak for the bulk metallic Ru. The shift to low binding energy values indicates the sintering of small Ru clusters under hydrogen exposure. The ruthenium oxide, responsible for the peak at a binding energy of 281.2–281.4 eV seen for the samples that were not reduced in the spectrometer, could be formed because of the oxidation of metallic Ru species by ambient air.

To analyze the Ru localization in the support layers, a depth analysis with a variation of the incident photon energy was performed. The change of  $h\nu$  from 400 to 1000 eV results in a variation of the kinetic energy of photoelectrons (KE) from 100 to 700 eV. According to the literature data, such a change of the KE leads to an increase of an inelastic mean free path ( $\lambda$ ) from ~4 to ~11 Å,<sup>[21]</sup> which defines the surface sensitivity of photoelectron spectroscopy.<sup>[22]</sup> The relative intensity of the Ru3d<sub>5/2</sub> line normalized to the intensity of the C1s line (I(Ru3d<sub>5/2</sub>)/I(C1s) ratio) might provide information on the particle localization. If the particles are localized inside the subsurface layers of the support, one might expect a decreased *I*(Ru 3d<sub>5/2</sub>)/*I*(C1s) ratio. However, the localization of the particles on the external surface of support should result in an increased  $I(Ru 3d_{5/2})/I(C1s)$  ratio. It is clear that at low KE values (100–300 eV) a decrease of the  $Ru 3d_{5/2}$  line intensity caused by the screening by the support would be more pronounced.

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Figure 4. Dependence of /(Ru 3d<sub>5/2</sub>)//(C1s) as a function of KE.

A dependence of the  $I(Ru 3d_{5/2})/I(C1s)$  ratios on the KE is shown in Figure 4. This ratio passes through a maximum for all samples, which indicates that the Ru clusters might be covered with a thin layer of carbonaceous species that shields the Ru signal. It is seen that the relative intensity of the  $Ru3d_{5/2}$  line increases with the increase in N content. The /(Ru 3d<sub>5/2</sub>)//(C1s) ratio for the Ru/6.8N-CNFs sample is substantially higher in comparison with other samples. To explain these results, it should be mentioned again that both the total Ru concentration and mean particle size of Ru (dispersion) on the support obtained by TEM are very close for all samples (Table 1). An analysis of the data indicated that there is no correlation of the intensity of the Ru signal with the porous structure of the N-CNFs supports (Table S1). As mentioned above, all used supports are mesoporous materials. Hence, the considerable increase of the Ru content in the surface layer of the samples with N can be explained by the stronger interaction of Ru with N sites on the external surface of the N-CNFs bundles that prevents Ru diffusion to the internal volume of the bundles and prevents the incorporation of Ru between graphene layers, which might take place in the undoped sample similar to that found for Pd/CNFs catalysts.<sup>[23]</sup> Therefore, a more uniform distribution of Ru through the support in the undoped sample should be expected. Such a binding of noble-metal clusters with N sites is in line with recent multiple results obtained by electron energy loss spectroscopy combined with scanning TEM.<sup>[10, 16, 24]</sup>

#### Formic acid decomposition

The conversion of the formic acid decomposition over the Ru catalysts with very similar metal charges, mean Ru particle sizes, but different contents of N in the support of 0, 2 and 6.8 wt% is shown in Figure 5a. The data demonstrate that the catalytic activity of Ru catalysts doped with N improves with the increased N-doping of the support. Thus, it is seen at 423 K that the Ru catalyst with the highest amount of N gives a conversion 1.5 times higher than that of the sample without N. Similarly, Marco et al.<sup>[6b]</sup> observed an approximately two times higher H<sub>2</sub> production for NH<sub>3</sub> decomposition over Ru



Figure 5. Temperature dependences of a) formic acid conversion over the Ru/N-CNFs catalysts and N-CNFs supports with different N contents and b) the selectivity of  $H_2$  production.

catalysts on monoliths covered with N-doped CNFs than on undoped samples.

A special long-term stability run was performed with the 1Ru/6.8N-CNFs catalyst for 25 h at 448 K (Figure S1). The change of the conversion during this run was small (from 33 to 29%). This experiment showed clearly the very high stability of the catalyst under the reaction conditions and confirmed that the binding of the Ru clusters to the N-CNFs support is strong and that Ru sintering is complicated.

Two supports without Ru were also studied for the formic acid decomposition to estimate whether there is a strong contribution from the support during the conversion of formic acid (Figure 5a). The support without N (0N-CNFs) was almost inactive for this reaction and showed less than 5% conversion at 573 K. The support with 6.8 wt% N showed a much higher activity that corresponds to 58% conversion at 573 K. The increased conversion over the support with N compared to that of the undoped support strongly indicates an improved activation of formic acid on the N sites. The obtained results allowed us to conclude that the conversion of formic acid with the Ru catalysts at 448 K was  $\approx$  30–50 times higher than that of the supports without Ru. Hence, the activities of the supports are very low compared to the activities of the Ru catalysts studied. However, the activation of formic acid on the N sites may also take place on the samples with Ru and has a positive influence on the catalytic activity.

The turnover frequencies (TOFs) for the total formic acid decomposition over the Ru catalysts at 373 K are shown in Table 1. At 373 K and under the same conditions, the Ru/CNFs catalyst without N demonstrated the same TOF (0.009 s<sup>-1</sup>) as the undoped Pt/CNFs catalyst with a mean particle size of 1 nm.<sup>[7]</sup> Solymosi et al.<sup>[13]</sup> obtained a comparable TOF  $(0.013 \text{ s}^{-1})$  under similar conditions for a 2 wt% Ru/C catalyst with a low metal dispersion (5.6%). However, they obtained a much higher TOF (0.064  $s^{-1}$ ) for a 2 wt% Pt/C catalyst with a dispersion of 23.5%. If our Ru samples were doped with 6.8 wt% N, the TOF almost doubled, whereas that of our Pt samples increased by an order of magnitude. The mean particle size of the Pt catalysts ( $\approx$ 1 nm) is smaller than that of the Ru catalysts ( $\approx$ 1.5 nm). Moreover, the Pt catalysts contained a substantial amount of atomically dispersed Pt and/or Pt clusters with a few atoms,<sup>[7]</sup> which can be active for formic acid decomposition in the presence of N on the support. This could explain the more pronounced effect of the N-doping for the Pt catalysts.

The selectivities to hydrogen do not change much with temperature (Figure 5 b). At 50% conversion for the 1.3Ru/ON-CNFs, 1.3 Ru/2N-CNFs, and 1Ru/6.8N-CNFs catalysts, the selectivities were 82.9, 87, and 91.5%, respectively. Hence, N incorporation in the N-CNFs structure improves the selectivity greatly. However, the selectivity of the Ru catalysts was lower than that of the Pt catalysts on the similar supports.<sup>[7]</sup> For the undoped Pt catalyst and the Pt catalyst with 7.5 wt% N, the selectivities at 50% conversion were 96.2 and 99.5%, respectively.

To understand whether the water gas shift (WGS) reaction contributes to the formic acid decomposition, this reaction was investigated for the 1.3Ru-6.8N/CNFs catalyst. It is important that no conversion of CO was observed over the temperature range of 473–593 K. Similarly, Basinska et al.<sup>[25]</sup> demonstrated that a 2 wt% Ru/C catalyst with a mean Ru particle size of 3.4 nm showed some activity but only at very high temperatures (623 K). This proves that there is no significant contribution from the WGS reaction to the formic acid decomposition over the Ru catalysts under the reaction conditions studied. Hence, the formation of CO<sub>2</sub> and H<sub>2</sub> from formic acid decomposition takes place in parallel with the formation of CO and H<sub>2</sub>O.

Arrhenius plots of the TOF values for the dehydrogenation and dehydration reactions calculated from the conversion and selectivity values are shown in Figure 6. For the dehydrogenation reaction, the TOF<sub>CO2</sub> values for 1.3Ru/0N-CNFs, 1.3Ru/2N-CNFs, and 1Ru/6.8N-CNFs catalysts at 373 K were 0.007, 0.009, and 0.014 cm<sup>-1</sup>, respectively, whereas for the dehydration reaction there was no significant difference in the TOF<sub>CO</sub> values ( $\approx 0.001 \text{ s}^{-1}$ ). These data show that N-doping promotes the formic acid decomposition reaction to the direction of dehydrogenation and does not affect the dehydration reaction. The apparent activation energies for the dehydrogenation and dehydration reactions over all the Ru catalysts were also calculated from the Arrhenius plots (Figure 6). The apparent activation energies are the same for both reactions in the range of 55– 58 kJ mol<sup>-1</sup> (Table 1).



**Figure 6.** Arrhenius plots for TOFs in formic acid dehydrogenation and dehydration reactions over the Ru/N-CNFs catalysts with different N contents.

We assigned the dependence of the  $TOF_{CO_2}$  and  $TOF_{CO}$  values on the N content to the appearance of a new route for the formic acid dehydrogenation that involves N sites on the support in the neighborhood of the metal clusters. Basic pyridinic N<sup>[15b]</sup> in the vicinity of the Ru clusters can form an adduct with formic acid [Eq. (1)]:

$$>$$
 N+HCOOH  $\rightarrow$  > NH<sup>+</sup>HCOO<sup>-</sup> (1)

The higher activity observed for the formic acid decomposition on the N-doped CNFs without Ru as compared to the undoped CNFs (Figure 5 a) may indirectly support the presence of such activation of formic acid on N-containing sites. The intermediate formed can interact with the Ru clusters to give H<sub>2</sub> and CO<sub>2</sub>, which thus provides an additional selective route to H<sub>2</sub> for formic acid conversion [Eq. (2)]:

$$> NH^{+}HCOO^{-} \xrightarrow{Ru} > N+H_{2}+CO_{2}$$
 (2)

The apparent activation energy for this reaction could be close to that for the reaction that takes place on metallic Ru. The rate of the dehydration reaction does not change in this case as it is determined by the surface sites on Ru clusters, which are same size for all the catalysts studied. The appearance of the new route that is selective to  $H_2$  leads to the observed increase of selectivity (Figure 5 b). As the interface of the Ru clusters and N sites of the support is not as contiguous as it was for the Pt catalysts with smaller clusters and the possible presence of isolated Pt atoms, the contribution of this route to the total conversion of formic acid for the Ru catalysts is smaller. In accordance, we observed a decrease of the effect of N for the Pt/N-CNFs catalysts with an increase of the mean size of Pt clusters from 1.0 to 2.0 nm.<sup>[7]</sup> Importantly, the proposed explanation based on the appearance of the new dehydrogenation route is also in line with the literature results for the liquid-phase formic acid decomposition with some homogeneous catalysts, which include Ru complexes.<sup>[3, 26]</sup> This shows that the addition of amines to the liquid accelerated the formic acid decomposition considerably. An alternative explanation based on the presence of sub-nm sized Ru species invisible by regular TEM can be also proposed. These Ru species may dehydrogenate formic acid only if they are coordinated by the N sites of the support.

## Conclusions

We have demonstrated that N-doped carbon nanofibers are promising catalyst supports for active Ru catalysts for the production of hydrogen from vapor-phase formic acid decomposition. The synthesized N-doped and undoped samples possessed approximately the same Ru content, mean particle size, and particle sizes distributions. Photoelectron spectroscopy data for the original samples showed that there are two Ru states in the samples: slightly charged or metallic Ru clusters and oxidized Ru species similar to those in RuO<sub>2</sub>. For the sample with the highest N content, the former Ru clusters are the main species. The Ru content on the external surface of the N-doped support is considerably higher than that of the undoped support. The increase of the surface metal concentration can occur as a result of the coordination of the Ru clusters by pyridinic N located on the open edges of graphene layers of the herringbone-type carbon nanofibers used. The strong binding of the Ru species with pyridinic N could prevent their diffusion into the internal volume. This allows the high accessibility of these clusters to formic acid as well as the possibility of an additional route for dehydrogenation by the activation of formic acid through the formation of adducts on the interfacial pyridinic N adjacent to the Ru clusters. As a result, the rate of the dehydrogenation reaction increases, whereas the rate of the dehydration reaction does not change. This leads to a considerable increase of the selectivity of the hydrogen production from 83 to 92%. The results obtained could be useful for the development of Ru/C catalysts for the transfer hydrogenation of biomass-related products with formic acid or alcohols.

## **Experimental Section**

## **Catalyst preparation**

N-doped CNFs were synthesized by the decomposition of a mixture of ethylene and ammonia on a 65 wt% Ni/25 wt% Cu/10 wt%  $\mathrm{Al_2O_3}$  catalyst at 823 K for 1 h as described previously.  $^{[9,15a]}$  The catalysts were prepared by coprecipitation from nitrate salt solutions. To obtain 0, 2, and 6.8 wt % N in the supports, the concentration of ammonia in the mixture was increased, which corresponded to 0, 50, and 75 vol %. To obtain the catalyst, all the obtained materials were treated with concentrated HCl several times over several weeks at RT and then with boiling 2 M HCl for 30 min. After this, the materials were washed with distilled water until no chloride ions were detected in the rinsing liquid. In spite of the harsh treatment in HCl, the presence of some Ni was observed in the catalysts by photoelectron spectroscopy and energy-dispersive spectroscopy (EDS) combined with TEM. Based on these studies and studies of the catalytic properties of the CNFs supports and Ru/N-CNFs catalysts, this Ni was assigned as encapsulated by carbon nickel carbide particles of a relatively large size (>10 nm) that are not accessible for interaction with the Ru precursor and formic acid. The observed encapsulation indicates that this Ni can have hardly any effect on the decomposition of formic acid.



Ru catalysts on the N-doped CNFs were prepared by deposition of Ru from aqueous solutions of Ru(NO)(NO<sub>3</sub>)<sub>3</sub> by the incipient wetness impregnation method.<sup>[9]</sup> After the impregnation, the samples were dried and reduced in flowing H<sub>2</sub> at 573 K for 2 h.

#### **Catalyst characterization**

The content of Ru in the samples was determined by X-ray fluorescence analysis by using an ARL Advant'x (Thermo Scientific) spectrometer. It was 1.3, 1.3, and 1 wt% for the samples that contained 0, 2, and 6.8 wt% N, respectively (Table 1). TEM measurements were performed by using a JEM-2010 (JEOL) instrument with an accelerating voltage of 200 kV. The size distributions of the Ru particles were calculated from the measurements of at least 300 particles.

High-resolution photoelectron spectra were recorded with synchrotron radiation at the BESSY II RGL station at Helmholtz-Zentrum in Berlin. The survey spectra were collected at an incident photon energy  $(h\nu)$  of 850 eV. The core-level spectra of C1s and Ru3d were recorded with a variation of the incident photon energy from 400 to 1000 eV. An incident photon energy of 800 eV was used to acquire the N1s spectra. The application of synchrotron radiation allowed the high-resolution acquisition of data in the 280-300 eV spectral region typical of Ru3d and C1s core-level lines, which thus allows the possibility to analyze the Ru state using the Ru 3d<sub>5/2</sub> spectra. For the scale calibration, the core-level line of metallic gold (Au  $4f_{7/2}$ ) with a binding energy of 84.0 eV was used as an external reference in all experiments. The spectra processing and analysis was performed using the XPS-Calc program after subtraction of the Shirley background.<sup>[15a,27]</sup> To shed light on the chemical state of Ru, additional measurements were performed after reduction of the Ru sample with the highest N content in the preparation chamber of the spectrometer. For this, the reduction in hydrogen at  $2 \times 10^{-2}$  mbar for 2 h at 623 K was undertaken. After the reduction, the preparation chamber was evacuated and the sample was transferred to the analysis chamber without contact with air.

The surface areas of the materials were calculated using the BET method from the data obtained by  $N_2$  adsorption at 77 K by using an ASAP-2400 instrument (Micromeritics).

#### Catalytic activity measurements

The vapor-phase formic acid decomposition was performed in a fixed-bed 4 mm id quartz reactor as described earlier.<sup>[28]</sup> Activity tests were performed at atmospheric pressure with 7 mg of catalyst placed between two layers of quartz wool. The catalysts were reduced in a 1 vol% H<sub>2</sub>/Ar mixture for 1 h at 573 K and cooled in He to the reaction temperature (333 K). To obtain a temperature dependence of the acid conversion, the composition of the outlet gas mixture was measured several times at each temperature (at least for 30 min) to ensure that steady-state was reached.

A controlled amount of formic acid (Sigma–Aldrich, 98–100%) was introduced into the system by using a syringe-pump (Sage) to obtain 1.9 vol% of formic acid vapor in He. The WGS reaction was performed using a 2.5 vol% CO/2.3 vol% H<sub>2</sub>O/He mixture. A total gas flow rate of 51 cm<sup>3</sup>min<sup>-1</sup> was used in all experiments.

The products were analyzed by using an HP-5890 gas chromatograph equipped with a thermal conductivity detector and Porapak-Q column. As no other carbon-containing products were detected, the conversion of formic acid was determined as the sum of the concentrations of CO and  $\mbox{CO}_2$  formed in each run and related to the initial concentration of formic acid.

Apparent activation energies and TOFs were calculated at low conversions up to 15%. The total TOFs were determined as the rate of the sum of CO and  $CO_2$  formation related to the number of surface metal sites calculated using the mean particle size values (TEM) with the Ru atomic area as 0.064 nm atom<sup>-1</sup>.

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