Ru/CNFs 催化剂催化氨分解制氢

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摘要: 研究了鱼骨式碳纤维 (CNFs) 和管式碳纤维 (CNTs) 负载 Ru 催化剂的氨分解反应活性。结果表明, Ru/CNFs 催化剂上氨分解活性高于 Ru/CNTs 催化剂。通过改变 Ru 负载量或载体表面的含氧基团来调节 Ru 的粒径。Ru 的活性位随着 Ru 颗粒尺寸的增大而增加。CNFs 上的含氧基团对 Ru 颗粒的氨分解活性影响很大。在相同粒径的 Ru 颗粒上, CNFs 表面的含氧基团增加了 Ru 的活性。

关键词: 碳纤维; 钌; 负载型催化剂; 氨分解; 氢气; 结构敏感性

中图分类号: O643

文献标识码: A

Carbon Nanofiber-Supported Ru Catalysts for Hydrogen Evolution by Ammonia Decomposition

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Abstract: Carbon nanofibers (CNFs) with fish-bone graphene alignment and carbon nanotubes (CNTs) were used to support ruthenium for ammonia decomposition. The Ru nanoparticles on the CNF supports are more active than those on CNT supports. The Ru particle size was adjusted by changing the Ru loading or by introducing oxygen containing groups onto the CNF surface. The site activity increases when the Ru crystal size increases. The oxygen groups on the CNFs have a remarkable effect on ammonia decomposition over the Ru nanoparticles. On identically sized Ru crystals, oxygen on the CNFs clearly enhances ammonia decomposition over the Ru/CNFs.

Key words: carbon nanofiber; ruthenium; supported catalyst; ammonia decomposition; hydrogen; structure sensitivity

Proton-exchange membrane fuel cells (PEMFC) have received plenty of attention because of their high energy-conversion efficiency and pollution-free emissions [1–3]. The production of hydrogen directly from carbonaceous substances, mainly hydrocarbons or alcohols, is limited because of the presence of CO in the hydrogen stream, which is difficult to remove and will degrade PEMFC performance. As an alternative route, ammonia decomposition is preferred for the production of CO_x-free hydrogen in PEMFCs because of a single feed stream, simple start-up, and low overall device weight and volume [4–6].

Ammonia decomposition has been extensively studied to

gain a better understanding of hydrogen production and also ammonia synthesis. Much research has been devoted to developing better catalysts, and Fe [7–9], Ni [7,10–14], and Ru [7,12,14–22] have been investigated. It has been found that Ru is the most active catalyst for ammonia decomposition. In general, support materials are used to increase the dispersion and stability of catalysts and the supports are reported to have different influences on Ru activity during ammonia decomposition. These influences depend on Ru particle sizes [21,22] or the electronic properties of the Ru particles [7]. Different supported Ru catalysts have been tested for ammonia decomposition and these include sup-

Received date: 6 April 2010.

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Foundation item: Supported by the National Natural Science Foundation of China (20776041), the Creative Team Development Project of Ministry of Education of China (IRT0721), and the 111 Project of Ministry of Education of China (B08021).

English edition available online at ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

ports of SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , activated carbon, and carbon nanotubes (CNTs) [7,12,14–20]. Among all the tested supports, the CNT supported Ru catalyst was found to be most active, and this has been attributed to the excellent electronic conductivity of the CNTs [7].

In addition to CNTs, carbon can form a number of other nano- and microstructures. Carbon nanofibers (CNFs) that have various and tunable nanostructures with graphene sheet orientations and thus different CNF edge structures have long been recognized as good catalyst supports [7,20,23–28]. They have frequently been employed as catalyst supports for selective hydrogenation [26,27] and dehydrogenation [27] because of their peculiar electronic properties. However, the effects of unique CNF edge structures on metal nanoparticles have not been explored during ammonia decomposition. The catalytic performance of Ru catalysts could possibly be optimized by fine-tuning the nano- and microstructures of the carbon materials.

In this study we investigate the decomposition of ammonia over CNF-supported Ru nanoparticles including the effects of the nanocarbon support structures, Ru crystal size, and CNF surface oxygen on the reaction to determine the site requirements of ammonia decomposition. The results show that the Ru/CNFs is a highly active catalyst for ammonia decomposition as a result of the peculiar surface properties of the CNFs, and this has not been reported previously in the literature.

1 Experimental

1.1 Catalytic synthesis of CNFs and CNTs

CNFs and CNTs were prepared in a fixed-bed quartz reactor by catalytic chemical vapor deposition (CCVD) onto iron nanoparticles and $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts, respectively, using CO as a carbon source [23]. The as-synthesized CNTs were first refluxed in 6 mol/L NaOH for 3 h under vigorous agitation to remove alumina. After reflux the sample was decanted, filtered, and washed with a large amount of deionized water. The CNFs and CNTs were further purified by 4 mol/L HCl to remove Fe and Ni. After repeating this purification procedure twice, the residues in the CNFs and CNTs contained less than 0.1 wt% Fe, 0.3 wt% Al_2O_3 , and 0.1 wt% Ni. Details of the purification procedures have been reported previously [23,24]. The purified CNFs and CNTs were then dried overnight at 120 °C in stagnant air, ground with a mortar, and sieved through a 160 mesh sieve. The CNF after purification is designated CNF-a.

To modify the surface characteristics of the CNF by removing surface oxygen it was annealed in Ar at 700 °C for 3 h and is designated CNF-Ar. To introduce more oxygen groups onto the CNF, CNF-a was treated with 4 mol/L

HNO_3 at 80 °C for 5 h, 30% H_2O_2 at 80 °C for 5 h, or stagnant air at 300 °C for 5 h, and these are designated CNF- HNO_3 , CNF- H_2O_2 , and CNF-Air, respectively.

1.2 Preparation of the Ru catalysts

CNF-supported and CNT-supported Ru catalysts were prepared by incipient wetness impregnation with an aqueous solution of ruthenium trichloride trihydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, Heraeus Corp.). The catalysts were first dried in stagnant air at ambient temperature for 12 h and then further dried at 120 °C for 12 h in an oven. The samples were stored in a sealed container. Before being used for ammonia decomposition, the catalysts were reduced at 300 °C for 5 h in a stream of 25% H_2 -75%Ar (360 ml/min).

1.3 Characterization of the samples

The textural properties of the CNFs and CNTs were characterized by N_2 physisorption on an ASAP 2010C (Micromeritics, USA) at –196 °C after out-gassing the samples at 190 °C and 133.3 Pa for 6 h. The microstructure and the morphology of the supports and supported Ru catalysts were studied with a JEOL JSM 2010 high-resolution transmission electron microscope (HRTEM) with an accelerating voltage of 200 kV and a point resolution of 0.18 nm. Suitable transmission specimens were prepared by the ultrasonic dispersion of the respective samples in ethanol, followed by a drop of the suspension being applied onto a holey carbon-coated copper grid. Ru dispersions were obtained according to the average size of Ru [29]. X-ray diffraction (XRD) was performed on a Rigaku D/Max 2550 VB/PC diffractometer using $\text{Cu } K_\alpha$ radiation.

1.4 Catalytic activity tests

Catalytic testing was carried out on a continuous flow quartz reactor (0.2 or 0.4 g catalyst) under a pure ammonia atmosphere at atmospheric pressure. A reactant stream of NH_3 (99.99%) was controlled with a calibrated mass flow controller. With H_2 as carrier gas, N_2 and unconverted NH_3 in the effluent gas were analyzed at room temperature using an online gas chromatograph (GC) with a thermal conductive detector (TCD) and a 3-m Poropak Q packed column. NH_3 fractional conversion was calculated by a standardized method on a nitrogen atom basis [10,11]. Blank tests indicated that ammonia conversion in the blank reactor or over the supports was less than 1% at 500 °C. In addition, no signals corresponding to CH_4 due to the methanation of carbon were detected, except for the 7.9 wt% Ru/CNFs catalyst. To illustrate that there was no mass-transfer limitation under the selected gas hourly space velocity

(GHSV_{NH₃}), two different catalyst loadings were used. The results showed that with a GHSV_{NH₃} of 6 500 ml/(h·g) the conversions were the same for the 0.2 and 0.4 g catalyst loadings indicating that the film diffusion resistance was negligible when the GHSV_{NH₃} was 6 500 ml/(h·g) or above.

1.5 Calculation of the activation energy and turnover frequency

It is widely accepted that the reaction kinetics for ammonia decomposition is [30]

$$-r_{\text{NH}_3} = k_+ \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{1.5}} - k_- \frac{P_{\text{N}_2} P_{\text{H}_2}^{1.5}}{P_{\text{NH}_3}}$$

In this study, the catalysts were tested at temperatures between 300–500 °C. At low temperature, the conversions are far from equilibrium conversions while at high temperatures, the equilibrium conversions are almost 100%. Therefore, the kinetics for ammonia decomposition can be simplified by neglecting the reversible reaction at relatively low conversions,

$$-r_{\text{NH}_3} = k_+ \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{1.5}}$$

The rate constant was obtained by applying a plug flow model to the reactor and fitting the experimentally determined ammonia conversion. The activation energy for each catalyst was obtained by Arrhenius plots.

Because the rate of ammonia decomposition depends on both ammonia and hydrogen concentrations, the reaction rates at 50% were selected for a rational comparison of the catalyst activities. The turnover frequency (TOF_{H₂}) of the reaction over the Ru catalysts was calculated using the reaction rate and the number of the exposed Ru surface atoms per gram of the catalyst. The average particle size was estimated by the equation $d_n = \frac{\sum n_i d_i}{\sum n_i}$ from Ref. [31] based

on TEM data. Ru dispersion was obtained using the equation $d_{\text{Ru}} = 1/d_n$ from Ref. [29] according to the average size of the Ru particles.

2 Results and discussion

2.1 Effects of nanocarbon structures

Ammonia decomposition was conducted over the

Ru/CNFs catalysts and the Ru/CNTs catalysts to determine the effect of nanocarbon structure on the reaction. The two representative HRTEM images in Fig. 1 show the obtained CNFs and CNTs. Individual CNFs and CNTs consisted of graphene sheets aligned in a definite direction to the fiber axis [23,24,28]. The graphene sheets with a cylindrical shape in the CNTs were parallel to the fiber axis while the sheets in the CNF were inclined, exposing their edges on the fiber surface. Therefore, the largest difference between the CNFs and CNTs is the edge structure.

Fig. 1. HRTEM images of CNFs (a) and CNTs (b).

The properties of the Ru catalysts supported on the CNFs and the CNTs are summarized in Table 1. Table 1 shows that the Ru/CNFs catalysts have a larger external surface area and pore volume than the Ru/CNTs catalysts, which is a result of more edge carbon atoms and therefore more defects on the CNFs surface. The Ru nanoparticles are highly dispersed on the surface of the CNFs with a mean particle size of about 1.0 nm, which is in line with our previous investigations [27,28]. The improved dispersion of the Ru nanoparticles on the CNFs is a result of the increased number of edge sites on the CNFs and they function as anchoring sites for the Ru nanoparticles [26–29]. The Ru/CNFs catalysts show very little change with regards to the Ru dispersion after an extended period of catalyst reduction. On the contrary, the Ru dispersion on the CNTs decreased remarkably when the reduction time was extended. This indicates a relatively strong interaction between Ru and CNFs compared with the interaction between Ru and CNTs.

Figure 2 shows the XRD pattern of a typical Ru/CNFs catalyst. The crystallinity of the CNFs is easily seen while no legible diffraction peaks associated with Ru are present. The absence of Ru diffraction peaks can be attributed to the high dispersion of Ru nanoparticles (< 2 nm) and the relatively low content of Ru in the catalysts.

Table 1 Properties of the Ru/CNFs and Ru/CNTs catalysts

Sample	Specific surface area (m ² /g)			Pore volume (cm ³ /g)		d_n /nm	Ru dispersion (%)
	BET	Micropore	External	Total	Micropore		
Ru/CNFs	180	23	157	0.36	0.009	1.0	100
Ru/CNTs	140	24	116	0.29	0.010	1.2	83

Fig. 2. XRD pattern of the 3.2 wt% Ru/CNFs.

The results in Fig. 3 clearly indicate that the Ru/CNFs catalysts are much more active than the Ru/CNTs catalysts. The mean particle size of the Ru nanoparticles (Table 1) is almost identical for both the CNFs and the CNTs. The difference in catalytic performance between the Ru catalysts is, therefore, dependent on the carbon support with different geometry configurations [7,23,24,26–28]. This leads to different electronic properties in the Ru nanoparticles since ammonia decomposition is very sensitive to the catalyst's electronic properties [21].

Figure 4 shows the NH_3 conversion over the Ru/CNFs and the Ru/CNTs catalysts for a time on stream of up to

Fig. 3. Comparison of NH_3 conversion (a) and TOF_{H_2} (b) as a function of reaction temperature over the Ru/CNFs and the Ru/CNTs. 0.4 g catalyst, $\text{GHSV}_{\text{NH}_3} = 6500 \text{ ml}/(\text{h} \cdot \text{g})$.

Fig. 4. Stability of the 3.2 wt% Ru/CNFs and the 3.2 wt% Ru/CNTs.

1 000 min, and this figure shows that both the Ru/CNFs and the Ru/CNTs are stable.

The reaction mechanism and microkinetics of ammonia decomposition have been studied in detail on $\text{Ru}/\text{Al}_2\text{O}_3$ [32]. Kinetic modeling has revealed that N_2 adsorption/desorption and at least one of the NH_x dehydrogenation reactions are part of the partial equilibrium and one of these reactions is the rate-determining step (RDS). The adsorption and recombination of N are normally very sensitive to the electronic properties of the Ru nanoparticles. This characteristic of the reaction has allowed ammonia synthesis to be used as a probe reaction for the electronic properties of the Ru nanoparticles on and inside the CNTs [33]. Because the kinetic relevant steps are similar in ammonia synthesis and in ammonia decomposition, ammonia decomposition can also be used as a probe reaction for the electronic properties of Ru nanoparticles. In this regard, a significantly higher TOF for Ru/CNFs compared with Ru/CNTs of almost an order of magnitude on Ru/CNFs at 450 °C compared with Ru/CNTs can be explained by the modification of the electronic properties of the CNF surfaces. Although both CNT and CNF are conductive, the peculiar surface edge structure must be responsible for the modification of the interaction between CNF/CNT and the Ru nanoparticles and thus the electronic properties. A detailed investigation of the electronic properties of Ru nanoparticles on different CNFs is an interesting subject for future study.

2.2 Effects of Ru crystal sizes

To verify the site requirement for ammonia decomposition, the reaction was investigated on different sized Ru crystals, which were obtained using different Ru loadings on the CNFs as shown in Table 2. The Ru crystal size increases with an increase in the Ru loading. The observed activity of the catalysts (Fig. 5) in terms of NH_3 conversion also increased with an increase in Ru loading. However,

Table 2 Ru dispersion and particle size from the TEM of the Ru/CNFs catalysts with different Ru loading

Ru loading (wt%)	Ru dispersion (%)	d_p /nm
1.0	100	0.8
3.2	100	1.0
5.5	55.6	1.8
7.9	47.6	2.1

when the Ru loading was increased to 7.9 wt% the methanation of the CNFs started. This most likely took place at the interface between the Ru and the CNFs. The TOF_{H_2} in Fig. 5(b) was higher on the Ru catalysts that had higher loading at all temperatures because of the larger crystal size (Table 2).

Fig. 5. Activities of Ru/CNFs catalysts with different Ru loading.

The apparent activation energy was measured on different sized Ru crystals to investigate possible changes in the reaction mechanism and the effect of crystal size on the rate-determining step. Figure 6(a) is an Arrhenius plot for the Ru/CNFs catalysts with different Ru loadings. Linear fits of the rate constants are all excellent except for the catalyst with a 7.9 wt% Ru loading possibly because of methanation that occurred on this sample. The activation energies and the TOF of the different sized Ru catalysts at 400 °C are plotted as a function of the Ru crystallite size (determined by HRTEM in Table 2) in Fig. 6(b). The apparent activation energy decreases slightly and the TOF_{H_2} increases as the Ru particle size increases, which indicates

Fig. 6. Arrhenius plots of the Ru/CNFs with different metal loading (a) and the activation energies as well as the activities of the prepared Ru catalysts at 400 °C (b).

that the Ru catalyst is structurally sensitive during ammonia decomposition.

B_5 -type sites in Ru catalysts have been recognized as being highly active for both the dissociation of N_2 and the association of N [16,17,21,22]. The B_5 -sites consist of an arrangement of three Ru atoms in one layer and two further Ru atoms in a lower layer. These are associated with steps and corners on the Ru nanoparticles. The B_5 -type site has also been reported as being important in ammonia decomposition by promoting the associative desorption of N^* atoms leading to N_2 formation [7,16,17]. However, it should be noted that the N^* atoms adsorb much more strongly on steps than on terraces. Our results suggest that some of the steps are blocked by very strongly adsorbed N^* and more step sites are blocked on the smaller crystals. This then explains the increase in TOF with an increase in the Ru crystal size. It is obvious that the optimized reaction rate compromises the strong adsorption of N atoms and their association to form N_2 . This is also the reason for the observed decrease in apparent activation energy with an increase in crystal size where the strongly bonded N^* increases the barrier for associative desorption.

The measured activation energy falls between 180–190 kJ/mol, which is much higher than the reported value (95–100 kJ/mol) on $\text{Ru}/\text{Al}_2\text{O}_3$ [32]. The desorption barrier

at the Ru(0001) terrace is 218 kJ/mol and 230 kJ/mol as obtained experimentally [17] and by density-functional theory (DFT) [16], respectively. The desorption barrier is much lower on the steps of Ru(0001) by about 120 kJ/mol as obtained by DFT [16], and this is not significantly different to the 145 kJ/mol obtained by fitting the measurements [17]. The measured activation energy is between that of steps and terraces but is closer to that of terraces and this is due to some steps being partially blocked during the reaction.

It can be concluded that an intermediate adsorption strength of N^* is required for ammonia decomposition to increase the associative desorption of adsorbed N^* . An optimized Ru crystal exists that possesses the correct specific surface area and fraction of steps.

2.3 Effects of CNF surface oxygen

Oxidative surface treatments of CNFs were conducted to investigate the effects of surface oxygen on the reaction and to improve the catalytic performance of the Ru/CNFs catalysts. From our previous work [24,27,28], different post treatments such as oxidation in air, H_2O_2 , and HNO_3 , and annealing in inert gas were performed to modify both the type and distribution of oxygen complexes on the CNF surface. After the gas phase oxidation, CNF has a higher concentration of carbonyl groups on the surface than the case after the liquid phase oxidation. In the latter case, carboxyls and anhydrides dominate. Among them, oxidation by HNO_3 introduced the largest amount of oxygen groups. As shown in Table 3, the surface areas of the CNFs treated with HNO_3 , H_2O_2 , and air increased by 28%, 12%, and 34%, respectively. In our previous work [24,27], this surface area increase was attributed to the existence of additional oxygen containing groups (mainly phenolic hydroxyl, carboxyl, and lactone groups) in addition to the defects on the CNFs surface.

Table 3 Results of ammonia decomposition over Ru/CNFs with different oxidation treatments (0.2 g catalyst)

Sample	$A_{BET}/(m^2/g)$	$TOF_{H_2}^a (s^{-1})$	Mean particle size ^b (nm)
Ru/CNFs-Ar	128	0.031	1.2
Ru/CNFs- HNO_3	164	0.150	2.2
Ru/CNFs- H_2O_2	144	0.082	1.8
Ru/CNFs-Air	171	0.046	3.7

^aDetermined with 3.2 wt% Ru catalysts at 400 °C and with $GHSV_{NH_3} = 13000 \text{ ml}/(h \cdot g)$.

^bDetermined by HRTEM.

The TEM images (Fig. 7) illustrate a rather uniform distribution of Ru nanoparticles for all the CNFs studied suggesting that CNF is a promising support to stabilize small

Fig. 7. HRTEM images and Ru particle sizes of Ru/CNFs with different surface treatments. (a) Ru/CNFs-Ar; (b) Ru/CNFs- HNO_3 ; (c) Ru/CNFs- H_2O_2 ; (d) Ru/CNFs-Air.

Ru nanoparticles. However, the modification of CNFs by oxidation seems to have resulted in an increase in the average diameters of the supported Ru particles (1.0–4.0 nm) compared with the Ru particles (about 1.0 nm) on the as grown CNFs without oxidation treatment as shown in Fig. 6 and Table 2. This is possibly due to the localized oxygen groups promoting metal aggregation. Larger Ru particles on the oxidized CNFs were also observed by Plomp et al. [34].

The TOFs of the Ru/CNFs catalysts are plotted in Fig. 8 to compare the Ru catalytic behavior on the CNFs with and without oxidation treatment. It is interesting to note that oxygen on the CNF surface enhances Ru activity for ammonia decomposition for crystals up to 2.2 nm in size. For the crystals with an almost identical size of 1.8 nm that were

Fig. 8. TOF_{H₂} as a function of average Ru size over the Ru/CNFs catalysts.

obtained from Ru (loading of 5.5%) on CNFs without oxidation and by oxidation with H₂O₂, the Ru/CNFs-H₂O₂ was found to have a much higher TOF than the catalyst that had raw CNF as a support. The effect of CNF surface oxygen on the reaction is more pronounced for the CNFs oxidized by HNO₃, as a maximum amount of acidic oxygen groups were introduced. However, Ru crystals of 3.7 nm in size have much lower activity than the crystals that are 2.2 nm in size. This is due to the concentration of the B₃ sites (dependent on Ru particle size) and the greatest probability of finding these surface ensembles is for particles of 1.8–2.5 nm in size [16,17,22]. The effect of surface oxygen on the catalytic behavior of ammonia decomposition has not been reported. As discussed above, ammonia decomposition can be used as a probe reaction for the electronic properties of the Ru nanocrystals. Results reveal that the electronic properties can be modified by the oxygen groups on the CNFs. This is attributed to the electron withdrawing property of oxygen containing groups on the CNF surfaces, e.g. phenolic hydroxyl, carboxyl, and lactone groups [35]. These groups lower the adsorption of N* and thus promote the associative desorption of N* to form N₂. These interesting topics should be a subject for a detailed future study.

In addition, Ru supported on annealed but non-oxidized CNFs has similar activity to the Ru nanoparticle catalysts that are supported on raw materials. It is known that annealing the CNFs at high temperature will increase the degree of graphite and thus the electrical conductivity of the CNFs [24]. This result indicates a weak or no dependence of Ru activity on the degree of graphite or the electrical conductivity of the nanocarbon support.

3 Conclusions

Our results clearly show that CNF-supported Ru nanoparticles are active catalysts for CO-free hydrogen

production by the decomposition of ammonia. We also found that ammonia decomposition is sensitive to the electronic properties of the metal nanoparticles, and this reaction can be used as a probe reaction to investigate the electronic properties of these nanoparticles. The activity of the Ru particles can be controlled by changing the particle size. The peculiar surface edge structure on the CNFs improves the electronic property of Ru and thus better activity is obtained for ammonia decomposition over the CNF than over the CNT support. The TOF increases and the apparent activation energy decreases with an increase in the Ru crystal size. Ammonia decomposition requires an intermediate N* adsorption strength. The electron withdrawing properties of the oxygen groups on the CNFs promote the associative desorption of N* thus increasing the catalytic activity of the Ru particles.

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