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Effect of Nitric Acid Treatment on Carbon Nanotubes (CNTs)-Cordierite Monoliths Supported Ruthenium Catalysts for Ammonia Synthesis

Xiujin Yu · Bingyu Lin · Binbin Gong · Jianxin Lin · Rong Wang · Kemei Wei

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Abstract Nitric acid treatment of CNTs-cordierite monolith changes the amount of Mg, Si, Al and oxygen-containing functional groups, thereby influencing on the surface area and pore size distribution of composite materials. Appropriate treatment of CNTs-cordierite with nitric acid increases the surface area and the amount of micropores slightly, but improves the activities for ammonia synthesis noticeable, which might be a consequent of the variation of the amount of Mg, Si, Al and oxygen-containing functional groups. The ammonia synthesis activity of Ba–Ru/CNTs-cordierite increase by more than 30% if the support material is treated at 30 °C for 4 h with nitric acid.

Keywords CNTs-cordierite · Nitric acid treatment · Ru · Ammonia synthesis

1 Introduction

Carbon nanotubes (CNTs) supported ruthenium catalysts have been reported showing excellent performance in ammonia synthesis [1–4] because CNTs have some special characteristics such as the high electrical conductivity, the high purity, the high graphitization of tube wall, and specific metal-support interactions. However, CNTs usually consist in powder form, and have some drawbacks such as agglomeration, difficulty of filtration and high pressure drop for gas phase operation [5], which limit the use of CNTs as catalyst supports in industry. To circumvent these drawbacks, a new method for CNTs application has been reported by incorporating CNTs into larger porous objects. Yin and co-workers [6] found that the MgO-CNTs nanocomposites were thermally more stable than CNTs in a H_2 flow and more efficient for the generation of CO_χ-free hydrogen from NH_3 decomposition as the supports of ruthenium catalysts.

The honeycomb cordierite monolith materials, which are mainly composed of MgO, Al_2O_3 and SiO_2 [7, 8], offer several advantages over other particulate supports, including of a high geometric external surface, structural durability, a low pressure drop, thermal shock resistance, and uniform flow distribution within the matrix [9]. However, these materials are not suitable for using as catalyst supports since they usually exhibit quite small specific surface area and weak metal-support interactions. Previous work of our group has found that CNTs-cordierite composition are promising candidates as support materials used in ammonia synthesis when CNTs were grown on cordierite [10]. Compared with those of bare cordierite monoliths, the surface area of CNTs-cordierite and the activities of Ba-promoted ruthenium catalysts for ammonia synthesis increase remarkably.

The as-prepared CNTs always contain large amounts of impurities, such as amorphous carbon and catalytic metal particles [11]. It was reported that reflux the CNTs in boiling nitric acid was one of the most commonly used purification methods [12, 13]. Furthermore, treating nanotubes with nitric acid could introduce a larger number of oxygen-containing functional groups such as carboxyl, lactones and phenols and create a more hydrophilic surface structure and [14–16], which were benefit for the dispersion of supported metals [17]. Giordano et al. [18] demonstrated that oxidized carbon nanotubes with nitric

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X. Yu · B. Lin · B. Gong · J. Lin · R. Wang (✉) · K. Wei
National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, 523 Gongye Road, Fuzhou, Fujian 35002, People's Republic of China
e-mail: rwang@fzu.edu.cn

acid led to the larger number of carboxylic groups generated, which was a consequent of, therefore, the obtained Rh/CNTs catalysts showed much smaller size and higher dispersion, resulting in better catalytic performance in liquid-phase hydrogenation and hydroformylation reactions. Similar phenomena also have been observed in other CNTs supported metals catalysts, such as Ag/CNTs [14], Co/CNTs [16], Ni-Cu/CNTs [19], Pt/CNTs [20] and Ni/CNTs [21]. Although these catalysts usually were used for the preparation of carbonaceous products in solution, the nitric acid oxidation method might be effective for improving our CNTs-cordierite composition supported ruthenium catalysts. However, it must be noted that oxidation of CNTs with nitric acid also can damage the structure of carbon atoms on the surface of the carbon nanotubes [22–24]. Moreover, nitric acid treatment led to the removal of Al and Mg ions from the silicate structure and subsequent generation of free amorphous silica on the surface of the cordierite [25], which are all disadvantageous for ammonia synthesis.

For clarifying the effect of nitric acid treatment on Ba–Ru/CNTs-cordierite monolith catalysts and further understanding the potential of CNTs-cordierite composite materials were used as the support material for Ru catalyst in ammonia synthesis, CNTs-cordierite monoliths were treated with nitric acid, and then the as-obtained materials were used as the supports for ruthenium catalysts, their physicochemical properties were characterized by X-ray fluorescence spectroscopy (XRF), N_2 adsorption, Scanning electron microscope (SEM), CO chemisorption and Temperature-programmed desorption (TPD), the catalytic activities were also examined and the influence of nitric acid treatment conditions was discussed.

2 Experimental

2.1 CNTs-Cordierite Monolith Preparation

Carbon nanotubes (CNTs)-cordierite monoliths were prepared according to reference [10]. Briefly, ø10 mm × 20 mm cordierite monolith blocks (300 cells per square inch, 0.7 m^2/g, obtained from Jiangsu Yixing Non-Metallic Chemical Industry Machinery Plant, China) were impregnated with $Co(NO_3)_3$ solutions. After withdrawal from the solution, excess solution was removed with pressurized air and then dried in air at 120 °C. The cobalt nitrate loading on cordierite was 0.3 wt%. The as-prepared samples were placed in a self-made boat positioned in the central position of a quartz tube within a horizontal tubular electric furnace, and first reduced in 25% H_2 in Ar (total flow rate 100 mL/min) at 500 °C for 2 h, then heated to 730 °C in acetylene and hydrogen gases (50 and 50 mL/min, respectively) for 20 min. Hydrogenation of the as-obtained materials were carried out at 750 °C for 2 h to removing a few percents of amorphous carbon.

2.2 Nitric Acid Treatment of Composite Materials and Preparation of Ru-Based Catalysts

The CNTs-cordierite monoliths were stirred in 65% HNO_3 and refluxed (the treatment conditions were showed in Table 1), then washed with water until neutrality. After drying at 120 °C for overnight, the samples were impregnated with $RuCl_3$ aqueous solution, dried and reduced in H_2/N_2 at 450 °C for 8 h, then cooled down to room temperature in N_2. The reduced Ru/CNTs-cordierite catalysts were impregnated with an aqueous solution of barium nitrate with a molar ratio of Ba:Ru = 0.5:1. The weight ratios of Ru to CNTs-cordierite were all ca. 4 wt%.

2.3 Characterization

XRF studies were carried out on a PANalytical Axios X-ray fluorescence spectrometer with a rhodium tube as the source of radiation. The samples were crushed and prepared to 30 mm diameter pressed pellets for analysis, the results were analyzed by IQ+ and then normalized to 100%, and composition were expressed as oxides. BET surface areas were measured by N_2 adsorption at −196 °C using Micromeritics ASAP 2020 instrument. The microstructures of CNTs were studied using scanning electron microscopy (SEM, JSM-6700F).

CO chemisorption was carried out with an AutoChem 2910 instrument (Micromeritics). Prior to chemisorption measurements, the samples (100 mg) were reduced in hydrogen (30 mL/min) at 300, 400 and 450 °C for 2 h, respectively, then flushed with helium (30 mL/min, 1 h) to remove adsorbed hydrogen and cooled down to room temperature in He. CO was injected at regular intervals until the area of the recorded peaks became constant, base

Table 1 Identification codes and treatment conditions of the various composite materials

Samples	Temperature (°)	Time (h)
CTC	–	–
$CTC_{30\text{-}0.5}$	30	0.5
$CTC_{30\text{-}1}$	30	1
$CTC_{30\text{-}2}$	30	2
$CTC_{30\text{-}4}$	30	4
$CTC_{30\text{-}8}$	30	8
$CTC_{60\text{-}4}$	60	4
$CTC_{90\text{-}4}$	90	4
$CTC_{90\text{-}8}$	90	8

on a CO:Ru stoichimetry of 1 [26], the chemisorption data were used for calculating the values of fractions exposed (FE or dispersion) and ruthenium particle size. TPD study was carried out using the apparatus described above for CO chemisorption experiments. The experiment was performed by sample heating at a rate of 10 °C/min from room temperature to 850 °C under a He flow (30 mL/min). The effluents (m/e = 28 for CO, 44 for CO_2) were monitored by an online mass spectrometer (Pfeiffer vacuum, OmniStar).

2.4 Activity Studies

The ammonia synthesis was performed in a stainless steel reactor, the catalysts were activated in a stoichiometric H_2 and N_2 mixture at 200, 300, 400, 425, 450, 475 and 500 °C for 24 h. After stabilizing under the reaction conditions (10MPa, 450 °C and 10000 h^{-1}) for more than 3 h, the ammonia concentration in the effluent was determined by a chemical titration method [26, 27].

3 Results and Discussion

Our previous result has showed that the carbon content of as-synthesis composite was ca. 17 wt% [10], the contents of other elements in CNTs-cordierite monoliths with nitric acid treatment are shown in Table 2. The cordierite is comprised of MgO, Al_2O_3, SiO_2 and small amount of other oxides such as CaO and TiO_2, therefore, Si, Al and Mg species would be leached out when cordierite is put in an acidic medium. Recently, Garcia-Bordeje et al. [28] pointed out that the basic character of Mg and Al would lead to Mg and Al was leached more easily with acids than Si. Form the Table 2, we can found that appropriate nitric acid treatment of CNTs-cordierite monoliths leads to the amount of Mg and Al decrease, while the content of Si would increase. When the CNTs-cordierite monoliths are treated with nitric acid at 90 °C for 8 h, the composite materials become brittle and fell to pieces after experiments, which might be as a result of too large number of Mg and Al was leached.

Table 2 Effect of nitric acid treatment conditions on the component (wt%) of composite supports

Sample	Al_2O_3	MgO	SiO_2	CaO	Fe_2O_3	Co_3O_4	TiO_2
CTC	44.61	10.25	40.78	0.49	1.26	0.12	2.49
$CTC_{30\text{-}0.5}$	44.46	9.43	41.02	0.77	1.51	0.11	2.70
$CTC_{30\text{-}1}$	44.45	9.36	41.20	0.72	1.21	0.10	2.96
$CTC_{30\text{-}2}$	44.05	9.43	41.06	0.74	1.38	0.11	3.23
$CTC_{30\text{-}4}$	44.27	9.46	41.37	0.64	1.22	0.08	2.96
$CTC_{30\text{-}8}$	42.78	9.07	42.19	0.94	1.79	0.16	3.07
$CTC_{60\text{-}4}$	43.04	9.69	41.43	0.90	1.45	0.11	3.38
$CTC_{90\text{-}4}$	40.34	8.73	45.82	0.72	1.23	0.08	3.08
$CTC_{90\text{-}8}$	32.87	6.28	56.12	0.62	1.04	0.05	3.02

Table 3 Effect of nitric acid treatments on texture properties of composite supports

Samples	S_{BET} (m^2 g^{-1})	Pore size (nm)	$V_{tot}(N_2)$ (cm^3g^{-1})
CTC	37.2	9.3	0.086
$CTC_{30\text{-}0.5}$	41.8	9.4	0.099
$CTC_{30\text{-}1}$	42.1	8.6	0.090
$CTC_{30\text{-}2}$	43.6	9.4	0.102
$CTC_{30\text{-}4}$	45.3	8.6	0.099
$CTC_{30\text{-}8}$	45.9	7.5	0.085
$CTC_{60\text{-}4}$	44.2	8.4	0.092
$CTC_{90\text{-}4}$	60.3	5.2	0.104

The specific surface area, pore size and pore specific volume of CNTs-cordierite monoliths are listed in Table 3. It can be seen that the surface area slightly increase with the increase of treatment temperatures and times, however, if nitric acid oxidized composite at 90 °C for 4 h, the data largely increase from 37.2 to 60.3 m^2 g^{-1}. The increase of surface area might be due to oxidation of CNTs with nitric acid was an effective method to remove the amorphous carbon, carbon black and carbon nanoparticles introduced by CVD preparation process, and then probe inner cavities of the CNTs, which exposed their internal surface area [12, 15]. Furthermore, the leaching of Mg and Al also should be responsible for the increase of surface area, therefore, the surface area of $CTC_{90\text{-}4}$ increase much more noticeable.

Pore size distribution of CNTs-cordierite with nitric acid treatment is shown in Fig. 1. The pore radius of CNTs (1.5–2.3 nm) increase with increasing the nitric acid treatment temperatures and times, in contrast, the pore radius about 10–40 nm decrease remarkable, which might due to Mg and Al are leached (Table 2).

Figure 2 shows the microstructures of CTC and $CTC_{30\text{-}4}$. SEM examination indicates that the CNTs on composite surface with acid treatment are much better in quality than that raw sample without treatment, which is in good accordance with previous results [12, 15, 29–31]. This result also further confirms above description that some amorphous carbon would be removed by nitric acid treatment.

Acidic oxidation treatment not only breaks carbon nanotubes by eliminating the amorphous carbon, but also introduces a more hydrophilic surface structure and a larger number of oxygen-containing functional groups such as carboxyl, lactones and phenols, these groups on carbon materials decompose upon heating by releasing CO and CO_2 at different temperatures, thus thermal desorption spectroscopy (TDS), also called TPD in a vacuum or in a

Fig. 1 Pore size distribution of the as-grown and oxidized CNTs-cordierite monoliths

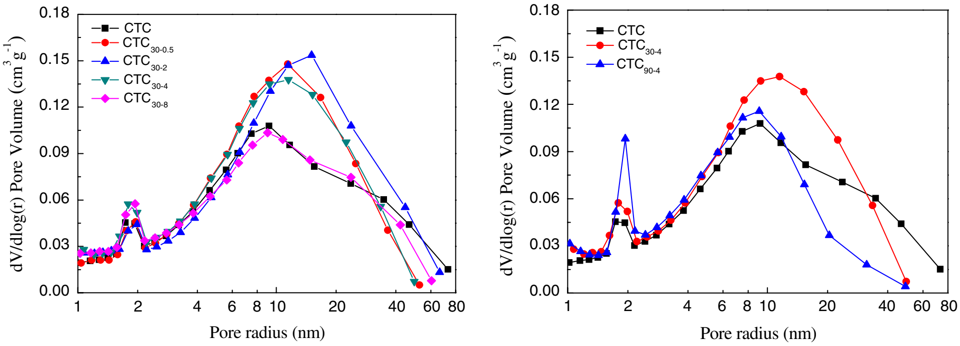
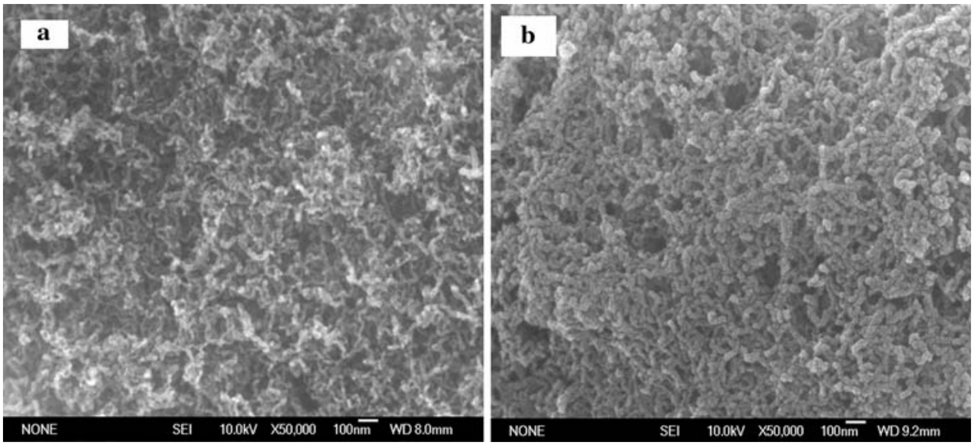


Fig. 2 SEM images of (**a**) CTC, (**b**) $CTC_{30\text{-}4}$



helium stream, could be used for the study of surface oxides [32, 33]. It has been widely accepted that each type of oxygen-containing functional groups decomposes to a defined product, e.g., a CO_2 peak results from carboxylic acids at low temperatures, or lactones at higher temperatures; carboxylic anhydrides originate both a CO and a CO_2 peak; phenols, ethers, and carbonyls (and quinones) originate a CO peak [32, 34–36]. The profiles of He-TPD show that the amount of CO_2 increase noticeable with the increase the treatment temperatures and times (Fig. 3a), indicating that the materials contain relatively more carboxyl and phenolic hydroxyl groups, and the severe treatment conditions might lead to more large much number of carboxylic acid groups generate. Unfortunately, it is difficulty to summarize the trend for CO from the TPD spectra (Fig. 3b), similar phenomena also has been observed because CO sometimes consist in an ascent without any clear maximum [36]. Some studies for further identifying the oxygen-containing functional groups are necessary.

Table 4 collects the CO chemisorption results of as-prepared Ba–-Ru/CTC catalysts, the ruthenium dispersion

Fig. 3 TPD profiles of composite materials with different treatment (**a**) CO_2 (m/e = 44) and (**b**) CO (m/e = 28)

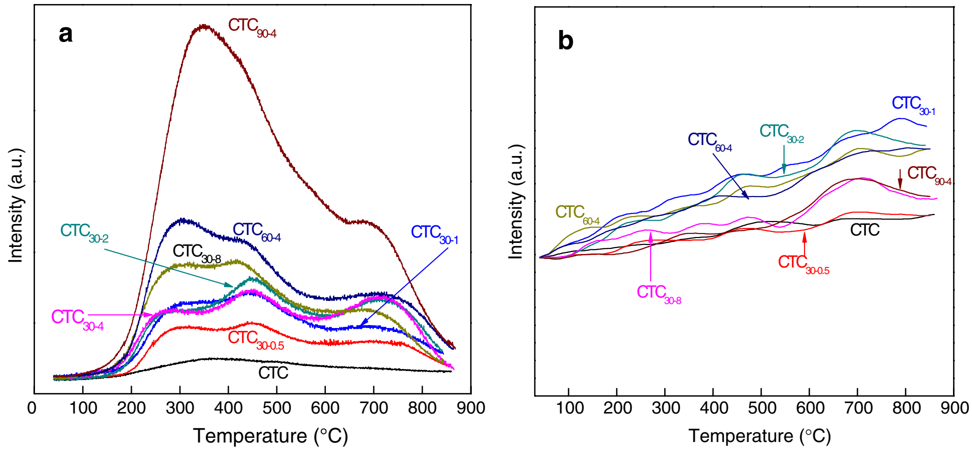


Table 4 CO pulse chemisorption characteristics of different Ru catalysts

Catalyst	CO uptake (cm^3/g STP)	Ru dispersion (%)	d(Ru) nm
Ba–Ru/CTC	3.15	40.6	3.3
Ba–Ru/$CTC_{30-0.5}$	3.50	45.1	2.9
Ba–Ru/$CTC_{30\text{-}1}$	3.50	45.1	2.9
Ba–Ru/$CTC_{30\text{-}2}$	3.57	46.0	2.9
Ba–Ru/$CTC_{30\text{-}4}$	3.57	46.0	2.8
Ba–Ru/$CTC_{30\text{-}8}$	3.50	45.1	3.0
Ba–Ru/$CTC_{60\text{-}4}$	3.51	45.2	2.9
Ba–Ru/$CTC_{90\text{-}4}$	3.80	49.0	2.7

increase significantly if the support materials are treated with nitric acid, thus the particle size of ruthenium metal decrease. However, the influence of treatment temperatures and times on the dispersion is slight. This can be easily comprehended considering that the texture character and hydrophilic surface of support materials both effect on the metal dispersion and particle size. The larger number of oxygen-containing functional groups is beneficial to the improvement of ruthenium dispersion [37]. However, according to the result of Kowalczyk [38], Ru crystallites (diameters typically several nanometers) are located mainly in large mesopores (diameters>3 nm). The high temperatures and the long times of nitric acid treatment lead to the amount mesopores in CNTs-cordierite monoliths decrease (Fig. 1), which is disadvantage for the dispersion of Ru particles. The particle size seems to be a good compromise between the opposite effects, thus the nitric acid treatment conditions influence slightly on the particle size of ruthenium metal.

From the Fig. 4, appropriate treatment of CNTs-cordierite with nitric acid could increase the activities for ammonia synthesis, for example, the activity of Ba–Ru/$CTC_{30\text{-}4}$ is 30% higher than that of Ba–Ru/CTC. However, the severe treatment conditions cause the decrease of the catalytic activities, which might be due to the amount of the leaching of Mg and Al on cordierite and carboxylic acid groups are too large. In general, the activity of the supported Ru catalyst decrease with the electronegativity of the compound increase [39]. Therefore, the activities of Ba–Ru/$CTC_{30\text{-}8}$ and Ba–Ru/$CTC_{90\text{-}4}$ are even much lower than that of Ba–Ru/CTC.

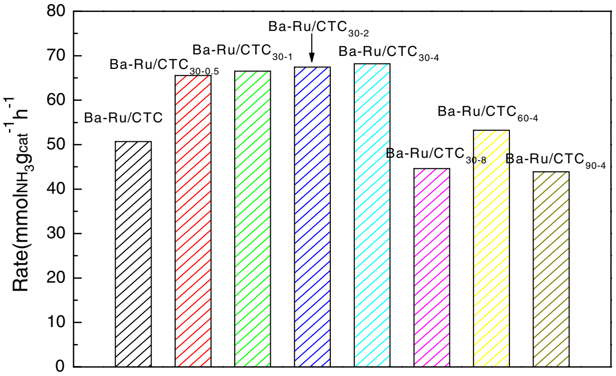


Fig. 4 Ammonia synthesis rates under 10 MPa, 450 °C, 10000 h^{-1} over various Ba–Ru/CNTs-cordierite monoliths catalysts

4 Conclusions

Nitric acid treatment of CNTs-cordierite monolith changes the amount of Mg, Si, Al and oxygen-containing functional groups, thereby influencing on the surface area and pore size distribution of composite materials. Appropriate treatment of CNTs-cordierite monoliths leads to the surface area and the amount of micropores increase slightly, some mesopores disappear and the stabilization of composite decreases if the treatment conditions are severe.

Nitric acid treatment under moderate conditions introduces more hydrophilic surface structure and a larger number of oxygen-containing functional groups, which are beneficial to improvement the dispersion of ruthenium metal and the activities for ammonia synthesis, the activity of as-supported ruthenium catalyst with Ba promoter increase by more than 30% if the CNTs-cordierite material is treated at 30 °C for 4 h, contrastly, the severe treatment conditions lead to the amount of the leaching of Mg and Al on cordierite and carboxylic acid groups are too large, therefore, the activities decrease noticeable.

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