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Preparation of Carbon Nanotubes (CNTs)-Cordierite Monoliths by Catalytic Chemical Vapor Deposition as Catalyst Supports for Ammonia Synthesis

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Abstract Tunable carbon nanotubles (CNTs)-coated monoliths as catalyst supports were prepared by catalytic chemical vapor deposition (CCVD) over deposited cobalt on cordierite. The influence of the preparation conditions such as the cobalt nitrate loading on the cordierite monoliths, the flow rate of reaction gases, reaction time and temperature on CNTs yield, thermal properties and structural features of the resulting materials were studied. The CNTs-cordierite was characterized by TEM/HREM, SEM, N_2 physisorption and TGA. The SEM showed that a relatively homogeneous mesoporous layer of CNTs covered on the surface of the cordierite monoliths. Comparing with the bare cordierite, the BET surface area and pore volume of CNTs-cordierite increased significantly. CNTs have penetrated into the cordierite substrate and led to a remarkable mechanical stability of the CNTs-cordierite monoliths against ultrasound maltreatment. The CNTs content, BET surface area, pore volume and thermal properties of CNTs-cordierite monoliths all could be changed by the variation of the synthesis conditions. Barium promoted ruthenium catalysts supported on the as-synthesized materials showed much higher activity for ammonia synthesis than their counterparts deposited on bare cordierite monoliths. Furthermore, the catalytic activity linearly increased with the BET surface area of CNTs-cordierite monoliths. The CNTs-cordierite monoliths were proved to be promising candidates as catalyst supports and the performance of catalysts supported on as-prepared materials would be easily modified by changing the growth conditions of CNTs.

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1 Introduction

Carbon materials attract a growing interest for using as supports in heterogeneous catalysis due to their specific characteristics such as the stability in acidic and alkaline media, the possibility to control the porosity and surface chemistry and the convenient recovery of precious metals [1–3]. Among different carbon materials, carbon nanotubes (CNTs) show excellent performance as the supports in various catalytic reactions including of hydrogenation reaction [4–5], selective dehydrogenation reaction [6], Fischer-Tropsch reaction [7] and ammonia synthesis [8–10] since CNTs have special characteristics such as the high electrical conductivity, the high purity, the high graphitization of tube wall, quantum effect and specific metal-support interactions. However, the carbonaceous supports have considerable disadvantages including of high cost and methanation under H_2 ambience [11]. Moreover, CNTs in powder form have some drawbacks such as agglomeration and difficulty of filtration due to the formation of fines for slurry phase operation and high pressure drop for gas phase operation [12], which limit the use of these materials as catalyst supports in industry. To circumvent these drawbacks, new method for CNTs application has been reported by incorporating CNTs into larger porous objects. Yin and co-workers [11] have found that the MgO-CNTs nanocomposites are 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. Janowska et al. [13] have grown CNTs on the wall of a silica reactor, which can be efficiently used as a catalyst support in liquid-phase reactions and indicated the great advantage of this support is the avoidance of catalyst-product separation.

The honeycomb cordierite monolith supports offer several advantages over other particulate supports, including of a high geometric external surface which is favorable for growing of CNTs, structural durability, a low pressure drop, thermal shock resistance, easy catalyst separation and uniform flow distribution within the matrix [14]. 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. Recently, Carbon nanofibres (CNFs) have been grown on alumina washcoated monoliths which have many potential applications as support materials [12, 15–17]. However, the alumina washcoat may be detached from the cordierite monoliths under operating conditions.

Our group [18] has synthesized CNTs-cordierite monoliths in situ via catalytic chemical vapor deposition (CCVD) of a C_2H_2:H_2 mixture over Fe catalyst. The CNTs-cordierites monoliths show the high BET surface area, suitable pore-size distribution and good attachment of CNTs to cordierite monoliths. The present study described about the preparation of CNTs- cordierite monoliths over cobalt catalyst and the growth condition such as the cobalt nitrate loading on the cordierite, the flow rates of the reaction gas, reaction time and temperatures were detailed investigated. The CNTs-cordierite monoliths were used as the supports of ruthenium catalysts for ammonia synthesis and the activities were studied to check the potential of CNTs-cordierite monoliths.

2 Experimental

2.1 Catalyst Preparation

The cordierite monolith supports were cut and trimmed into small blocks with ø10 mm × 20 mm (300 cells per square inch, obtained from Jiangsu Yixing Non-Metallic Chemical Industry Machinery Plant, China). Cobalt was introduced by impregnation of block cordierite monoliths in Co $(NO_3)_3$ solution. The cobalt nitrate loading on monoliths was in the range from 0.1 to 0.7 wt.% (based on the weight of original substrates). After withdrawal from the solution, excess solution was removed with pressurized air [19] and then the solvent was evaporated and dried in air at 120 °C.

2.2 Carbon Nanotubes Growth

Carbon nanotubes were grown over deposited Co on cordierite monoliths by acetylene decomposition according to literature [18] where Fe was applied as catalyst. The monolith was placed in a self-made boat positioned in the central position of a quartz tube within a horizontal tubular electric furnace. The catalyst was first reduced in 25% H_2 in Ar (total flow rate 100 mL/min) at 500 °C for 2 h in a CCVD furnace and then heated to a target temperature and flowed through with the reaction gas (C_2H_2:H_2) for a certain amount time. To remove a few percent of amorphous carbon, hydrogenation of the sample was carried out at 750 °C for 2 h [20–22].

2.3 Characterization of the Carbonaceous Materials

The carbon nonotubles (CNTs) yield was determined by weighting the sample before and after the various preparation steps. The microstructures and morphologies of CNTs were studied using scanning electron microscopy (SEM, JSM-6700F) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN). N_2 adsorption-desorption was performed on a NOVA 4,200e (Quantachrome Corp) instrument. The pore volume was calculated from the adsorbed volume at a relative pressure of 0.99. The specific surface area, the pore size distribution and the micropore volume were calculated by BET, BJH and t-plot method, respectively. Thermal analyses were carried out in a thermogravimetric analyzer (Perkin Elmer TGA 7). The temperature was elevated from room temperature up to 800 °C by 10 °C /min in 30 mL/min of air.

2.4 Preparation of Ru-Based Catalysts and Catalytic Activity Measurements

Ru-based catalysts were prepared by impregnation in the solution of $RuCl_3$. Before the impregnation, the CNTs-cordierite monoliths were stirred in 65% HNO_3 under reflux condition at room temperature for 2 h, washed with water until neutrality, and then dried overnight at 120 °C. For comparison, equivalent ruthenium (4 wt.% Ru) is introduced to various supports in this study. The CNTs-cordierite monoliths-supported Ru was dried at 120 °C overnight in air and reduced in H_2/N_2 at 450 °C for 8 h and then cooled down to room temperature in N_2. The reduced Ru/CNTs- cordierite monoliths were then impregnated with an aqueous solution of barium nitrate with a molar ratio of Ba:Ru = 0.5:1. The ammonia synthesis activity was measured in a stainless steel reactor. Before activity testing, the catalysts were activated in a stoichiometric H_2:N_2 mixture for 24 h and then stabilized under the reaction conditions, i.e. 10 MPa, 450 °C and 10,000 h^{-1} for more than 2 h. The ammonia concentration in the effluent was determined by a chemical titration method [23].

3 Results and Discussion

3.1 Experimental Conditions for the Synthesis of Carbon Nanotubes (CNTs) on Cordierite Monoliths

As shown in other CCVD production of CNTs, reaction conditions are the key to the successful generation of these materials [21, 24–26]. Previously, some results [24, 25, 27] showed that the plausible reaction mechanism would involve the adsorption and decomposition of acetylene molecules on the surface of Co nanoparticles dispersed on the support surface. Subsequently, the carbon atoms dissolve and diffuse into the nanoparticle interior to form a metal–carbon solid solution. Nanotube growth occurs when supersaturation leads to carbon precipitation into a crystalline tubular form. The tube continues to grow away from the particle by the deposition of the carbon on the contact region segment. The above-mentioned steps show that the steady-state growth process is a delicate balance between the dissociation of the carbon containing gases, carbon diffusion through the particle, and the rate of nucleation and formation of graphitic layers. Therefore, when the balance is disturbed, the CNT growth stops. The rate of carbon deposition was too fast and thus deactivation of the catalyst. Consider the hydrocarbon CVD process in its most basic form:

$$C_mH_n + \text{Carrier gases} \leftrightarrow C_d + (n/2)H_2 + \text{Carrier gases}$$

From this perspective, according to Le Chatelier's principle, the rate of carbon deposition should increase with increasing hydrocarbon concentration and decrease with increasing H_2 concentration. Therefore, the carrier gases (Ar, N_2 and H_2) are necessary for decreasing hydrocarbon concentration and thus depressing the rate of carbon deposition.

The morphologies of CNTs on monoliths with argon and hydrogen as carrier gases are showed in Fig. 1, Part of CNTs on cordierite monoliths entangled very tightly and thus partial cordierite was not covered with CNTs when argon was used as carrier gas, which is in contrast to the uniformity of the CNT layer in the cordierite monolith derived from the hydrogen used as carrier gas. According to Zhu et al. [28], hydrogen was used as carrier gases and they pointed out that hydrogen in the gas mixtures is to reduce the amorphous carbon formation and assist in the production of DWNTs during the CCVD process. In addition, Wasel et al. [29] suggested that hydrogen is to reduce the rate of carbon production by dehydrogenation so that the more ordered and thermodynamically stable MWCNTs can be produced rather than less ordered and thermodynamically stable soot and carbon fibers. Above phenomenon might appear in our study, in such a case, Hydrogen can eliminate or regenerate carbon-containing materials ($CH\chi$), which is favor for cleaning the surface of catalyst and suppressing carbon deposition. Meanwhile, it also provides another way to transfer carbon-containing materials from one side of catalyst particle (gas-solid interface) to another side (metal–carbon interface). In addition, it can increase stability of CNTs by combining with dangling bond of carbon atom in the edge of graphite plane, and thus CNTs on cordierite monoliths uniformly entangled with each other.

As mentioned above, the variation of the flow rates ratio between acetylene and hydrogen gases also affect significantly on the yield of CNTs produced. Our preliminary study show that the rates were 50 and 50 mL/min for acetylene and hydrogen gases respectively may be maintained during the reaction to obtain the maximum yield. Any variation of these flow rates (C_2H_2:H_2), viz.: (1) 10:90 mL/min; (2) 20:80 mL/min; and (3) 40:60 mL/min, lead the CNTs yield decreased (not shown). Therefore, the rates of acetylene and hydrogen both are 50 mL/min in this study.

The CNTs-cordierite monoliths retain their mechanical strength when the growth is carried out at the lower cobalt nitrate loading, i.e. 0.1 wt.% and 0.3 wt.%, while the

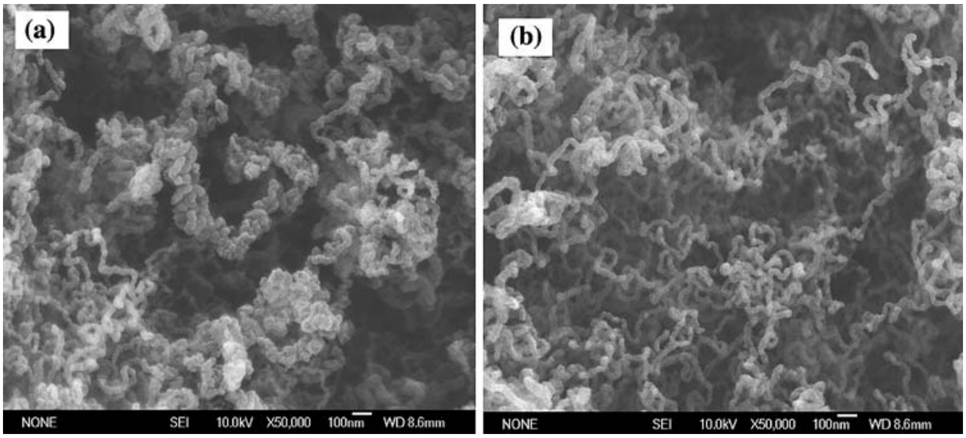


Fig. 1 Effect of the carrier gases on the morphology of CNTs on monoliths: (**a**) Ar; (**b**) H_2

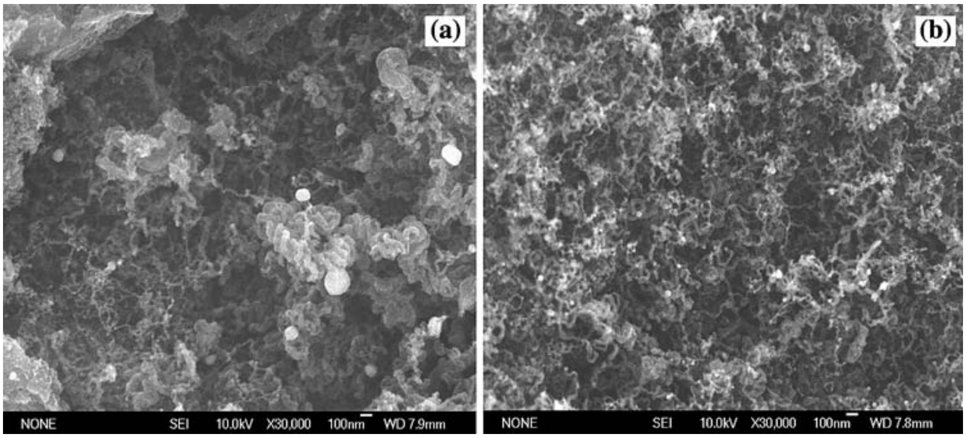


Fig. 2 SEM images of the CNT layer grown at 700 °C for 10 min over cobalt with different cobalt nitrate loading: (**a**) 0.7 wt.%; (**b**) 0.3 wt%

loading is high (0.7 wt.%), the CNTs-cordierite monoliths become brittle and fell to pieces after experiments. Figure 2 shows the SEM images of the CNTs-cordierite monoliths grown with cobalt nitrate loading of 0.3 wt.% and 0.7 wt.%. It is observed that the distribution of tubes diameter size is un-uniform and part of cordierite monolith wall is not covered with CNTs when the loading is 0.7 wt.% (Fig. 2a), which is in contrast to the uniformity of the CNT layer in the cordierite monolith derived from the 0.3 wt.% cobalt nitrate loading (Fig. 2b). It was suggested that the fragmentation in the cordierite would occur only when too many tubes are formed locally that cannot be hosted in the macro-pores [16]. The nanotubes can hardly escape from the macropores of the cordierite if the initial growth rate is too high, and CNTs impose stress in the cordierite wall thus affect the integrity of the cordierite structure [12]. Obviously, a precise control of cobalt nitrate loading on cordierite monoliths is crucial to preserve the excellent mechanical strength.

Table 1 collects the CNTs yield and the texture parameters of CNTs-cordierite monoliths synthesized with different cobalt nitrate loading at 730 °C for 20 min. It shows that when the cobalt nitrate loading (0.1–0.7 wt.%) increase, the BET surface area and pore volume both increase firstly and then decrease contrarily. It seemed that the porosity of the monoliths is relative to the pores between the entangled CNTs. When the cobalt nitrate loading is too high (0.3–0.7 wt.%), the CNTs yield increase and too much tubes may block the pores, and thus the pose size and porosity decrease (Fig. 3). The pore of the CNTs-cordierite monolith is mainly in the range of 4–30 nm.

Figure 4 shows the derivative weight loss of the CNTs grown with different time (5–40 min) in TGA experiment. The narrow peak at high temperature (ca.675 °C) of CNTs-cordierite monoliths grown with 20 min indicates that carbon is mostly graphitic and the amounts of amorphous carbon is negligible since it has been suggested that activated carbon with amorphous structure was always oxidation below 600 °C [30], which in agreement with the observations from SEM and TEM characterization. Fig. 4 also shows that the maximum oxidation rate of CNTs grown at 5 min is much lower than those grown at longer time, which may be ascribed to several factors such as the more disordered structure of these nanotubes, the lower yield of nanotubes on monoliths (Table 2), or some Co catalyst is not encapsulated when yield of nanotubes on monoliths is lower and therefore may catalyze the oxidation [30]. Another notable peak is showed in the profile of the monoliths grown at longest time (40 min), which might be ascribed to the oxidation of the pyrolytic carbon impurities. These pyrolytic carbon impurities arises form acetylene pyrolysis and may block the pores formed by entanglement of CNTs. Therefore, although the carbon productivity on cordierite monoliths increases, the BET surface area and total volume both do not increase significantly if the CNTs grown at 40 min (Table 2).

Table 1 The CNTs yield and the texture parameters of CNTs-cordierite monoliths synthesized over Co catalysts with different cobalt nitrate loading ($T = 730$ °C, $t = 20$ min)

Catalyst/support ratios (wt.%)	Yield Y_C (wt.%)	BET S.A (m^2g monolith^{-1})	V_{tot} (cm^3g monolith^{-1})	Pore size (nm)
0.1	11	29.1	0.11	7.73
0.3	16	41.9	0.13	5.81
0.5	18	34.5	0.10	5.90
0.7	–	15.6	0.04	4.60

–, the CNTs weight was not detected since the monolith has broken

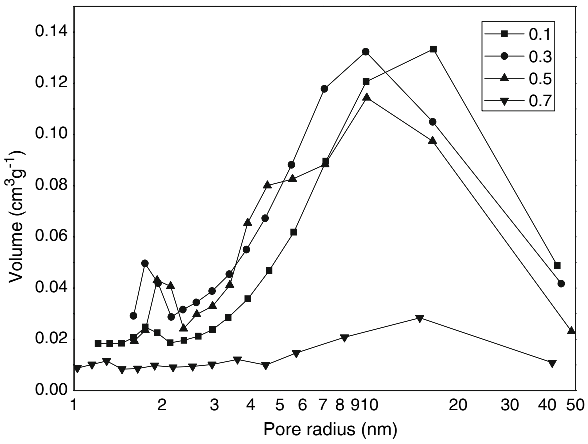


Fig. 3 Pore size distribution (PSD) curves CNTs-cordierite monoliths grown at different cobalt nitrate loading at 730 °C for 20 min

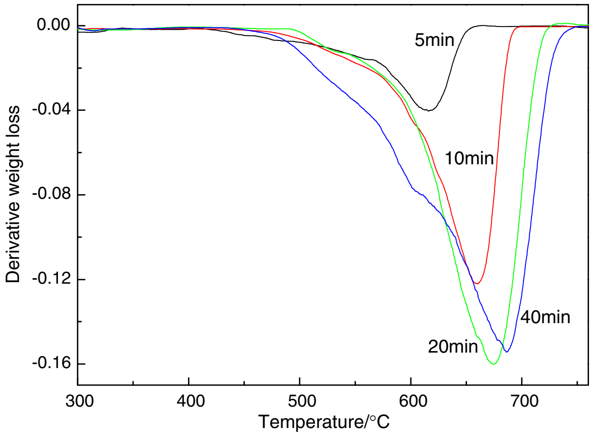


Fig. 4 Derivative of the weight loss of CNTs-cordierite monoliths grown at 700 °C for different time (the cobalt nitrate loading is 0.1 wt%)

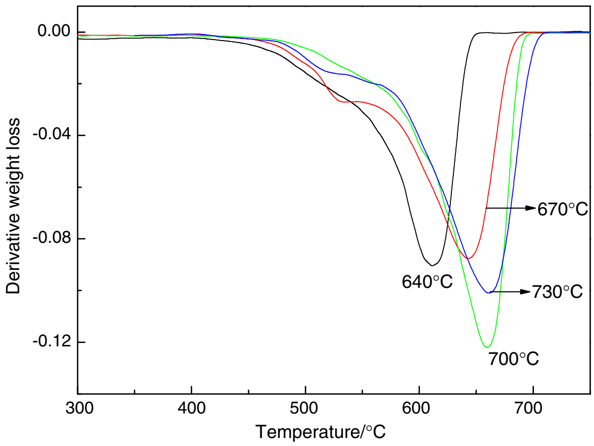


Fig. 5 Derivative of the weight loss of CNTs-cordierite monoliths grown at different temperatures ($t = 10$ min and cobalt nitrate loading = 0.1 wt%)

According to Ianov et al. [21], the graphitization of carbon into the tubular structures on metal-supported catalysts is generally accompanied by the formation of amorphous carbon. In the range of 500–800 °C, both processes are depended on temperature. In this case, Lower synthesis temperature (630–670 °C) results in lower CNTs yield and poorer CNTs quality. In contrast, the quality and yield of CNTs and the mount of pyrolytic carbon all increase with temperature (700–730 °C, which has been confirmed by the TGA experiments (Fig. 5). However, the formation of CNTs in these conditions is a very rapid process, thus the influence of thermal pyrolysis leading to the formation of amorphous carbon is slight, although a sight peak exhibits in the profile of CNTs-cordierite with reaction temperature at 730 °C.

3.2 Properties and Morphology of the CNTs-Cordierite Monoliths

Figure 6 shows the high-resolution TEM (HRTEM) of a segment of CNTs after nitric acid treatments where tubular layered structures could be resolved with a hollow cavity [21, 25, 26, 30, 31]. The tubes have uniform inner diameter of ∼5 nm and external diameter of ∼25 nm which is good agree with SEM images (Fig. 7b). There are lots of surface defects, i.e. edges and steps, on the graphene sheets which are suited for catalyst anchoring.

Figure 7 shows the representative SEM micrographs of bare and as-synthesized CNTs-coated cordierite monoliths. It is clearly seen that a homogeneous layer of CNTs up to 750 nm (Fig. 7d) form over cordierite monolith surface. The open structure of the cordierite monoliths would be sufficiently filled with CNTs, and the channels remain open. Moreover, the CNTs are coiled and entangled with each other which may be caused by the anisotropic catalytic activity of metal particles [18, 32]. There is little

Table 2 Results of CNTs synthesis on different reaction time at 700 °C and the cobalt nitrate loading is 0.1 wt.%

Growth time (min)	Yield Y_C (wt.%)	BET S.A (m^2g monolith^{-1})	Pore size (nm)	V_{tot} (N_2) (cm^3g monolith^{-1})
5	3	12.9	6.8	0.04
10	8	24.7	7.2	0.09
20	11	29.8	8.9	0.13
40	16	28.9	8.7	0.12

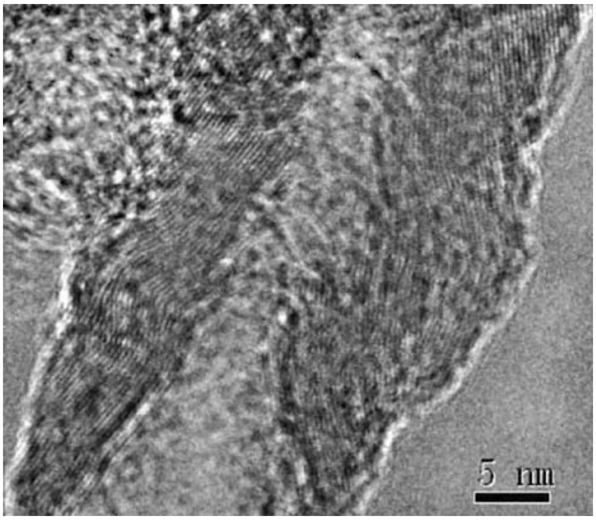


Fig. 6 HRTEM image of a typical segment of CNT. Growth conditions: 0.3 wt.% cobalt nitrate loading, $T = 730$ °C, $t = 20$ min

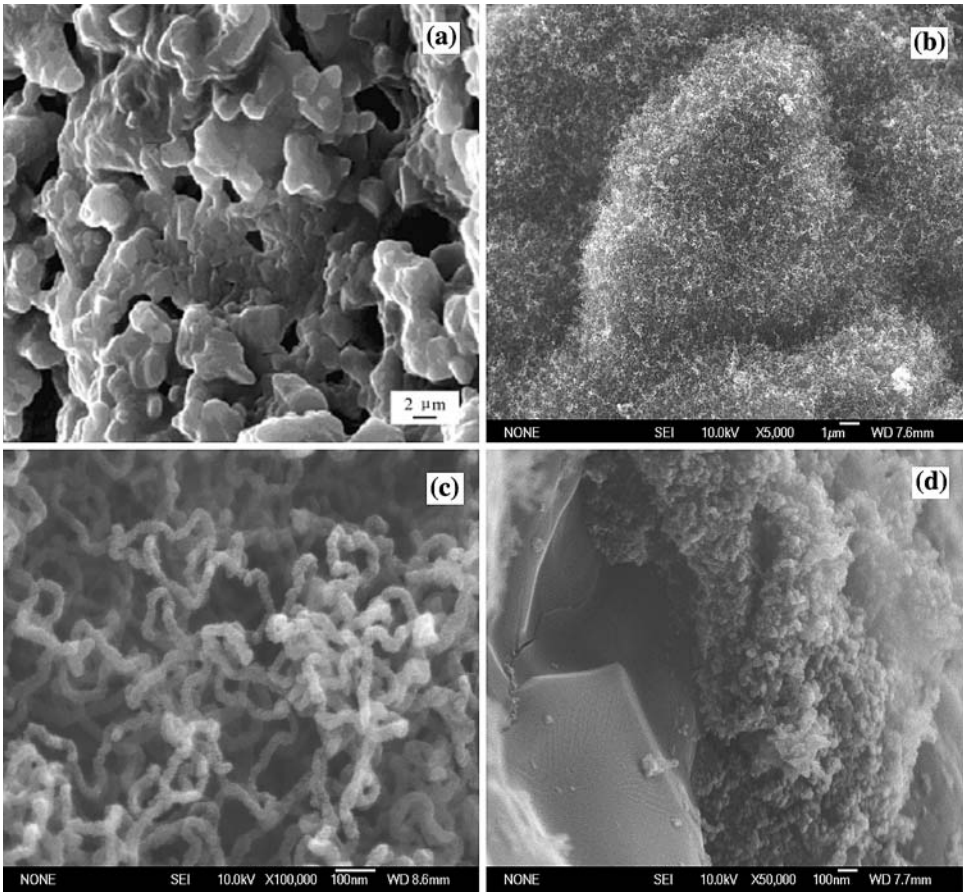
amorphous carbon (Figs. 6 and 7c), which is the result of hydrogenation at 750 °C for 2 h according to previous papers [20–22]. That is the reaction rate of amorphous carbon hydrogenation is significantly higher than that of graphitic carbon.

The strength of the attachment of the nanotubes was investigated by monitoring the weight losses after treatment in an ultrasonic bath for various durations (Fig. 8). After 30 min in the ultrasonic bath, the amount of CNTs in the cordierite monolith decreased from 19.18% to18.54% and leveled off at this value for prolonged treatments (up to 2 h). This confirms the strong anchoring of the nanotubes to the cordierite monolith and the nanotubes may have penetrated into wall which is consistent with the previous result [15, 18].

3.3 Activity of the Catalysts in the Ammonia Synthesis

It is necessary to add alkali or lanthanide promoters for enhancing the catalytic activity since the un-promoted Ru/carbon catalysts were shown to be rather inactive [33]. For comparison, equivalent barium is introduced to various catalysts in this study. The activities of the Ba-Ru/CNTs-cordierite monoliths catalysts with different supports are shown in Table 3. It shows that the ammonia synthesis activity of ruthenium supported on CNTs-cordierite monoliths is greatly higher than those on bare cordierite monoliths (more than 10 times higher), and the activity of

Fig. 7 SEM images of carbon nanotubes-cordierite monoliths (0.3 wt.% catalyst loading, $T = 730$ °C, $t = 20$ min): (**a**) bare cordierite; (**b**) fragments of cordierite occluded by nanotubes; (**c**) high resolution SEM of carbon nanotubes; and (**d**) side-view on monolith wall



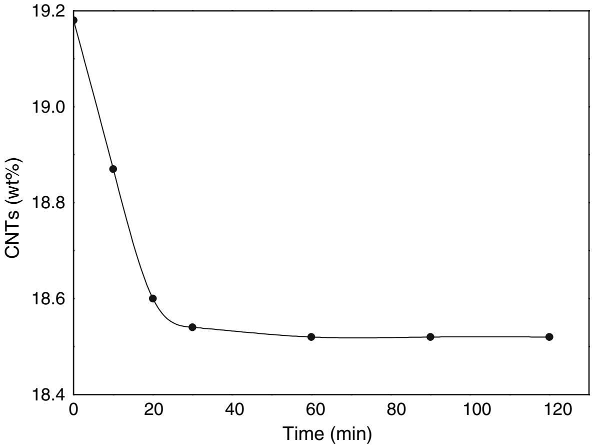


Fig. 8 Stability of CNTs attachment against ultrasound (40 kHz) treatment

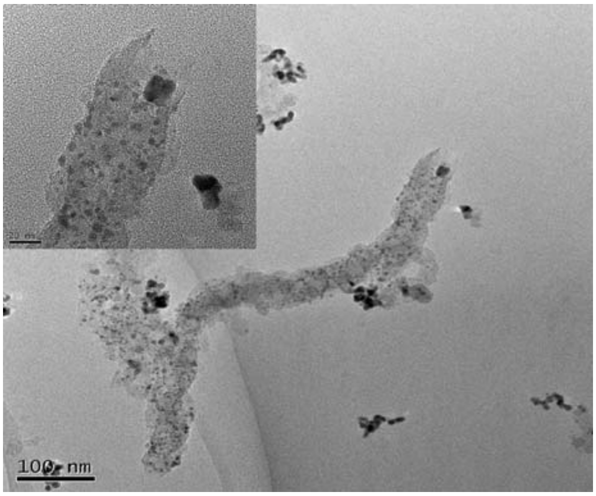


Fig. 9 TEM images of ruthenium catalysts supported on support "F"

Table 3 Activities of Ba-promoted CNTs-cordierite monoliths-supported Ru catalysts for ammonia synthesis

Sample	Yield Y_C[a] (wt.%)	BET S.A[a] (m^2g monolith^{-1})	NH_3 (vol%)[c]
A[b]	0	0.7	0.83
B	3	12.9	5.51
C	8	24.7	6.87
D	11	29.1	7.58
E	18	34.5	8.26
F	16	41.9	9.31

[a] Carbon yield and BET surface area data was obtained for composites supports before impregnation

[b] Bare cordierite monoliths were applied as supports

[c] Reaction conditions: 10 MPa, 450 °C and 10,000 h^{-1}

catalysts increased linearly with the BET surface area of the supports. The reason may be that the higher BET surface area allows a better dispersion of the metallic phase. Moreover, there may be many surface oxygen groups like carboxylic groups attached to the defective sites of CNTs after nitric acid treatments [34, 35]. These groups may react with ruthenium chloride to form the surface species of ruthenium. The stronger interaction between Ru and CNTs among these species may favor the uniform distribution of ruthenium and thus promote the ammonia synthesis activity [8]. Figure 9 is the TEM images of the Ru–Ba–CNT–Cordierite catalyst supported on support F. It shows that the ruthenium nanoparticles were mostly dispersed uniformly on the surface of CNTs. And the mean particle size of ruthenium is about 3 nm, which may be favor for formation of B5 sites [36], and thus the catalyst had high activity.

In a word, CNTs-cordierite monoliths might be promising candidates for the use as catalyst supports and it is possible to control the growth conditions for improving the performance of the CNTs-cordierite monoliths-supported catalysts.

4 Conclusions

This work described the preparation of monolith catalyst supports coated with a uniform mesoporous layer of CNTs of relatively small diameter via CCVD over deposited Co on cordierite. Both the growth conditions and the cobalt nitrate loading have a pronounced impact on the properties of the resulting CNTs-cordierite monoliths. Comparing with bare cordierite monoliths ($\sim$7 m^2g monoliths^{-1}), BET surface area ($\sim$40 m^2 g monoliths^{-1}) and pore volume ($\sim$0.13 cm^3 g monolith^{-1}) increase significantly, and the CNTs-cordierite monoliths have a great stability against ultrasound (40 kHz) treatment.

The CNTs-cordierite monoliths were tested as the supports of Ba-promoted ruthenium catalysts for ammonia synthesis. The activities were much higher than that of bare cordierite monoliths supported ruthenium catalyst, and increased linearly with the BET surface area of supports. In conclusion, rational design of catalysts and experiments can lead to an excellent CNTs-cordierite monolith as support materials.

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