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Preparation of Ni/MgO catalysts for carbon nanofibres by a self-propagating low temperature combustion process

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Ni/MgO catalysts were prepared using nitrate salt and citric acid in various ratios by the sol-gel self-propagating, low temperature combustion process. The products were characterized by the scanning electron microscopy, X-ray diffraction, thermogravimetric analysis and differential scanning calorimetry. The results show that Ni/MgO catalyst precursors of various particle sizes can be obtained by controlling the amount of citric acid. The catalytic activity of Ni/MgO decreases as the calcination temperature increases, owing to the difficulty of the NiO reduction. The mechanism of formation of Ni/MgO catalysts has also been proposed. Self-propagation combustion has great advantage of occurring at low temperatures, and the Ni/MgO is a suitable catalyst for low cost preparation of carbon nanofibres.

Keywords: *Ni/MgO catalyst; self-propagating combustion; sol-gel method*

1. Introduction

The availability of a catalyst of high activity and low cost is a key factor for the preparation of bulk-quantities of carbon nanofibres by the catalytic chemical vapour deposition (CVD) method. Generally, Fe, Co and Ni are used as the catalysts, owing to their large specific surface area. However, these nanoscale metal catalysts have great disadvantages, such as high cost and low catalytic activity, due to the conglomeration [1, 2] and difficulty with recycling [3]. Catalyst supports are the most effective way to improve catalyst activity. The catalyst may be highly dispersed onto supports,

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*Corresponding author, e-mail: nwfs@sina.com and may decrease conglomeration. Research on the use of Al_2O_3, SiO_2 and MgO as the supports showed that the catalytic activity and reaction time may be improved [4–6]. Among various supports, MgO has the advantage of being easy to remove during the purification of the as-grown carbon nanofibres [7, 8]. Therefore, great interest has been devoted to the study of MgO as a catalyst support in the preparation of carbon nanofibres by the catalytic CVD method.

Magnesium oxide is a kind of good alkali catalyst support, while metallic nickel has catalytic activity at low temperature. Therefore, Ni/MgO catalyst offers excellent potential for the preparation of carbon nanofibres owing to its high activity, selectivity and low cost [9, 10]. An Ni/MgO catalyst may be fabricated in two main ways, namely by the co-precipitation or the sol-gel method. Using the co-precipitation, Ni/MgO catalyst precursors may be produced by high temperature sintering of the hydroxide precursor of Ni/MgO obtained from mixed solutions of $Mg(NO_3)_2$, $Ni(NO_3)_2$ and KOH [11–15]. Ni/MgO catalyst precursors can also be fabricated by sol-gel method sintering of citrate gel obtained from mixed solutions of $Mg(NO_3)_2$, $Ni(NO_3)_2$ and citrates [9,16–18]. The co-precipitation is not suitable for fabrication of Ni/MgO catalyst precursors in bulk quantities, due to a long time of syntheses. On the other hand, the synthesis may easily be controlled by the sol-gel method and can also be conducted on a large-scale. In addition, Ni/MgO catalyst precursors must be calcined at temperatures higher than 700 °C, which makes the process more costly. At the same time, a higher calcination temperature is necessary to obtain NiO–MgO solid solution, with NiO diffusing into the MgO lattice which restricts the NiO to be reduced [19]. A strong oxidation-reduction reaction occurs when heating the organic salt gels, or organic salt and metal nitrate. The reaction releases an abundance of heat which can maintain the reaction space, resulting in formation of oxide powders; the method is known as the sol-gel self-propagating combustion method [20, 21]. The method has the advantage of having a low ignition point (150~250 °C) and it can produce powders which have high specific surface areas. It is a low temperature self-propagating combustion process, in contrast with a high temperature self-propagating combustion process [22].

In the paper, we report on the synthesis of Ni/MgO catalysts, using citric acid as the reduction agent and $Mg(NO_3)_2$ and $Ni(NO_3)_2$ as the oxidation agents, by a simple sol-gel self-propagating low temperature combustion process at ca. 250 °C. The influence of the ratio of citric acid to nitrate salt on the particle size of the catalyst precursors, and the role of the temperature on the sintering property of the catalysts, have been analysed in detail. The Ni/MgO catalyst powders synthesized by the low temperature self-propagating combustion process were compared with the powders that had been synthesized by direct calcination at higher temperatures. A formation mechanism of the Ni/MgO catalyst precursors synthesized by low temperature self-propagating combustion process is also proposed. The results show that the method takes great advantage of simple apparatus and the synthesis process in which the particle size of the Ni/MgO can be controlled. This therefore makes it a suitable method for the synthesis of catalysts of carbon nanofibres.

2. Experimental

The catalyst precursors were synthesized by the sol-gel self-propagating low temperature combustion process. Stoichiometric quantities of $Ni(NO_3)_2{\cdot}6H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ with molar ratios of Ni to Mg of 2:1, and molar ratios of nitrate salt to citric acid of 1:1, 1:2, 1:3 and 1:4 were mixed and fully dissolved in a given amount of distilled water, and then stirred for 2 h at 20 °C. Then water was removed in an oven at 90 °C until green gel-like products were formed. The yellow-green foam products were further formed by heating them in an oven at 200 °C for 30 min and then at 250 °C in a crucible, to form grey-black Ni/MgO precursor powders. In addition, the foam products were also calcined in air for 2.5 h at 600 °C, 700 °C and 800 °C. The final powder products were then obtained by pulverizing these calcined products.

Scanning electron microscopy observations were performed using a JEOL JSM-5600LV (15 KV) field emission scanning electron microscope. The X-ray diffraction patterns were obtained using a Siemens D5000 X-ray diffractometer with graphite monochromatized CuK_α radiation (λ = 1.5406 Å). The samples were scanned at the rate of 0.05 deg/s in the 2θ range of 10–80°. Thermogravimetric analyses and differential scanning calorimeter measurements were performed using a STA449C (Netzch, Germany) in air at the ramp rate of 2 deg/min.

3. Results and discussion

The thermogravimetric and differential scanning calorimeter (TG/DSC) curves of the Ni/MgO catalyst precursor gels are shown in Fig. 1. The molar ratios of nitrate salt to citric acid were 1:1 (sample A), 1:2 (sample B), 1:3 (sample C) and 1:4 (sample D). Figure 1a shows the TG curves for samples A–D, which are labelled accordingly. The combustion process for samples A and B initially starts at 200 °C but it becomes more dramatic for A at 270 °C and for B at 350 °C. The TG curves for C and D differ significantly from those for A and B, and exhibit weight loss at 200 °C and 350 °C, respectively, with the increase in the amount of citric acid. According to the DSC curves (Fig. 1b), the exothermic peak increases noticeably at 270 °C for sample A, and very small exothermic peaks occur at 350 °C for samples B, C and D. Therefore, thermal decomposition of Ni/MgO catalyst precursor gels can be explained as occurring in the stages as follows:

- The endothermic process in the DSC curves corresponding to evaporation of water in the gels and fusion of the gels between 70 °C and 200 °C.
- The organic complex compounds decompose from 200 °C to 350 °C, releasing an abundance of heat. However, the change in this stage is closely related to the quantity of citric acid. The gel powder A (1:1) decomposes quickly at 270 °C showing the

exothermic peak on the DSC curve. The weight losses of B and C gels increase dramatically at 350 °C with very small exothermic peaks. This is considered to be mainly attributed to the lower energy requirement for the decomposition of the dissociative carboxylic acid and carboxylic acid salt compared with the energy requirements for gels with higher contents of citric acid. In particular, an endothermic peak at 200 °C is also clearly observed when the molar ratio of the nitrate salt to the citric acid is up to 1:4, which may be caused by the decomposition of the excessive dissociative carboxylic acid. The combustion time at 200 °C increases, and the excessive citric acid of the C and D gels is considered to be partially responsible for this.

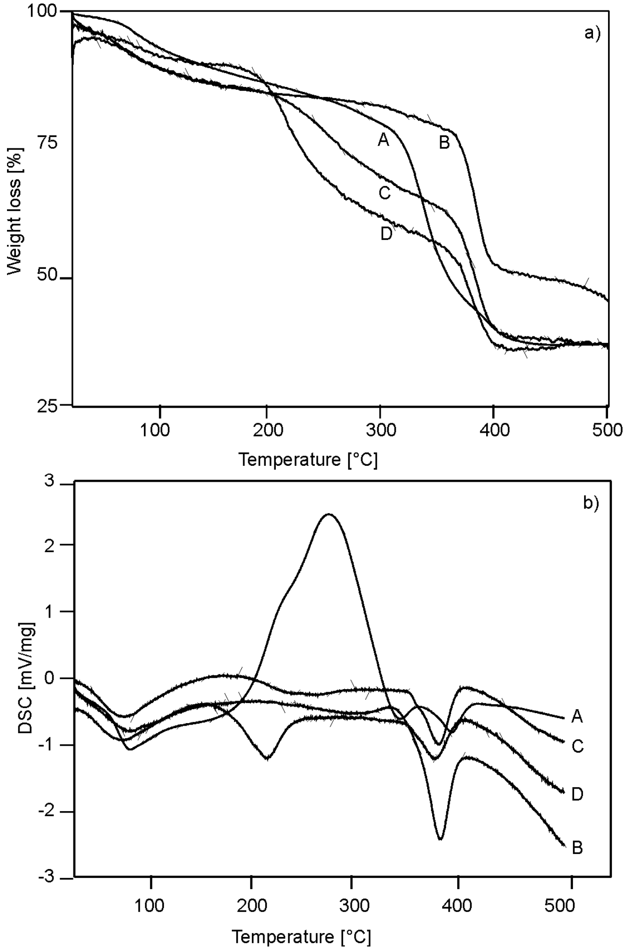

Fig. 1. TG (a) and DSC (b) curves of the catalyst precursor gels

- Ni/MgO catalyst powders form at temperatures higher than 350 °C. The weight losses of gels C and D increase dramatically, owing to the decomposition of the excessive citric acid, according to the TG curves. Thermal decomposition of the catalyst precursor gels is complete above 400 °C.

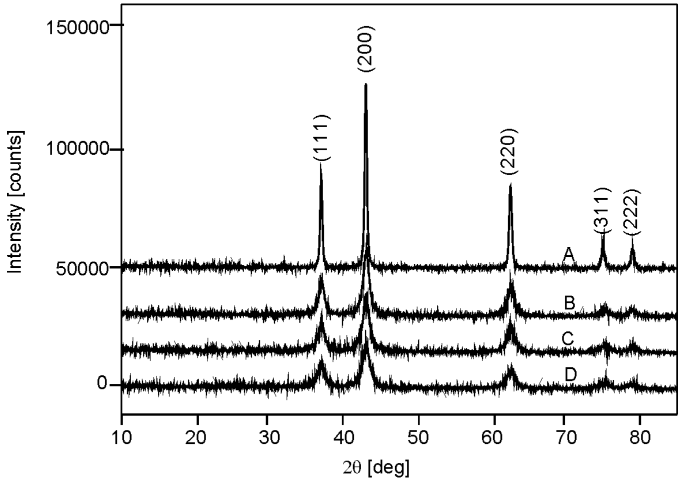

Fig. 2. XRD patterns of the gels with various ratios of nitrate salt and citric acid after self-propagating combustion: A – 1:1, B – 1:2, C – 1:3, D – 1:4

X-ray diffraction (XRD) patterns of the gel powders with various ratios of nitrate salt to citric acid and produced by self-propagating combustion are shown in Fig. 2. $Ni_xMg_{1-x}O$ solid solution can be formed from MgO and NiO at random proportions owing to the fact that the lattice parameters of MgO and NiO are similar to that of the NaCl crystal, and that the ionic radii of Mg^{2+} and Ni^{2+} are very close (0.65 Å and 0.70 Å, respectively). The diffraction peaks of the samples can all be indexed to Ni/MgO solid solution by consulting the data given in the Joint Committee on Powder Diffraction Standards (JCPDS) card for Ni/MgO solid solution (JCPDS 24-0712). The diffraction intensity of the Ni/MgO solid solution decreases significantly and the diffraction peaks broaden with the increase in the proportion of citric acid in samples A to D. The crystalline size of the samples also decreases in inverse proportion to the quantity of citric acid; the average crystalline sizes of samples A to D were calculated, using the Scherrer formula, to be 26.7 nm, 23.75 nm, 19.43 nm and 15.8 nm, respectively.

Scanning electron microscopy (SEM) images of the samples A–D obtained by the self-propagating combustion process are shown in Fig. 3. Ni/MgO catalysts display particle structures with distinct interfaces among the particles. The particle size evidently decreases as the proportion of citric acid increases. The average particle size is highest, reaching the value of 100 nm with an uneven size distribution when the molar ratio of the nitrate salt to citric acid is 1:1. However, the particles have the average size of only 20 nm and a uniform size distribution if the molar ratio of nitrate salt to citric acid is decreased to 1:4.

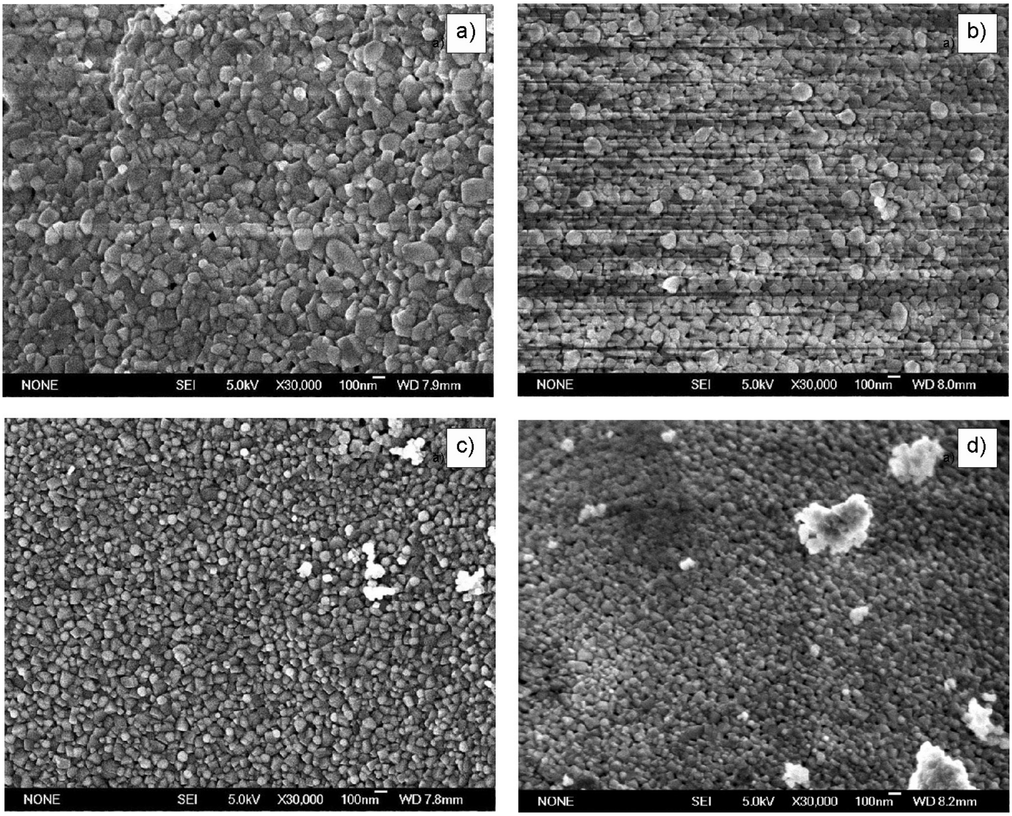

Fig. 3. SEM images of the gels with different ratios of nitrate salt and citric acid after self-propagating combustion: a) 1:1, b) 1:2, c) 1:3, d) 1:4

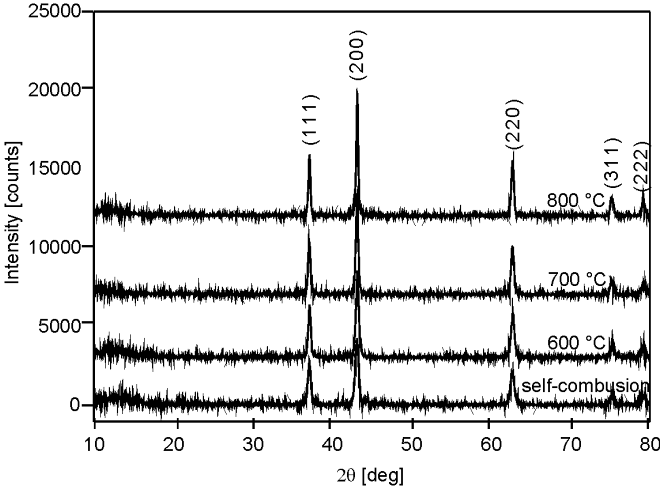

Fig. 4. XRD patterns of the catalyst precursor gel sample B with the molar ratio of 1:2 obtained by a self-propagating combustion process and calcination at various temperatures

Figure 4 shows the XRD patterns of the catalyst precursor sample B (1:2) obtained by self-propagating combustion and calcination at 6 various temperatures. The crystalline structures of the samples are the same as that of NaCl crystal, according to the XRD patterns. The diffraction intensity of the samples increases upon increasing calcination temperature. The results show that Ni/MgO catalyst precursors can be obtained by self-propagating combustion of gels without high temperature heat treatment.

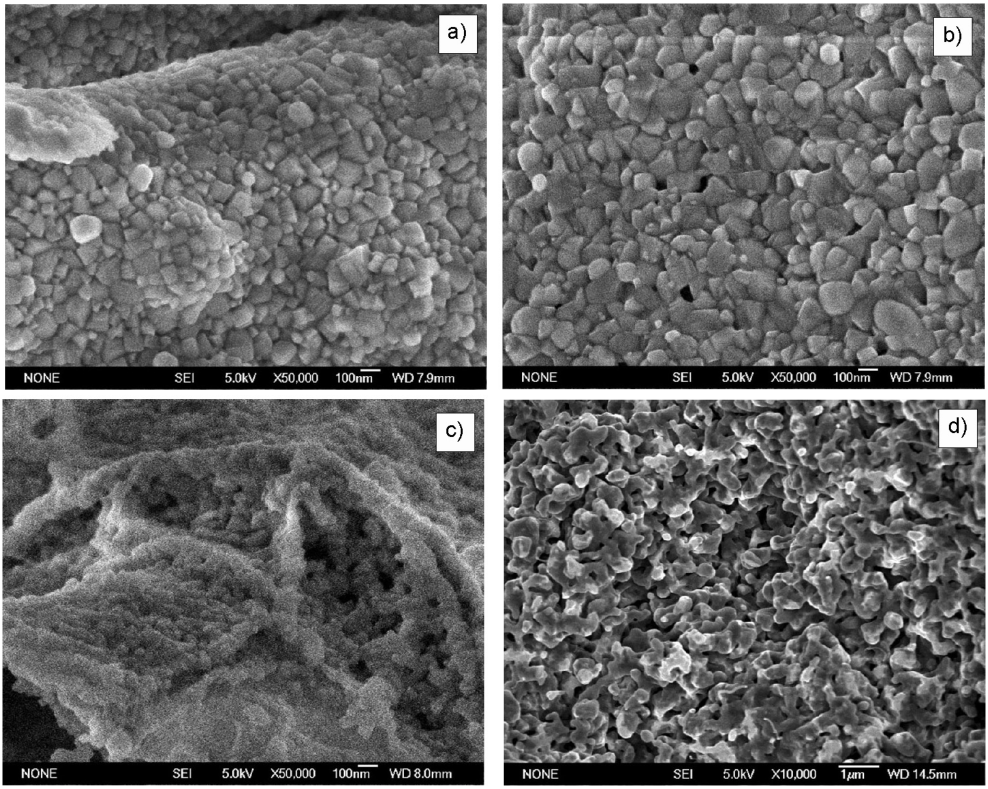

Fig. 5. SEM images of the gels B (1:2) after calcination at various temperatures:
a) 600 °C, b) 700 °C, c) 800 °C, d) heat treatment Ni at 600 °C

Figure 5 shows the SEM images of samples B calcined at various temperatures. Compared with Fig. 3b, the products maintain an excellent dispersive state. Regular prismatic and spherical structures with obvious crystal interfaces can be observed in the sample calcined at 600 °C (Fig. 5a). The particle size increases and the particles become deformed after calcination at 700 °C (Fig. 5b). Finally, particles with irregular morphology appear if the sintering temperature is increased to 800 °C (Fig. 5c). The crystal interfaces are obscure and the specific surface areas of the samples also decrease. Therefore, the catalyst precursors can be aggregated by increasing the calcination temperature; this can lower the catalytic activity of the Ni/MgO powders. The sintering property of the Ni/MgO catalyst powders is also analyzed by making comparisons with nanoscale Ni powders that had been produced without support (Fig. 5d). The specific surface area of the nanoscale Ni powder increases dramatically upon increasing particle size due to the surface effect. It results in an increase of the surface energy. The nanoscale Ni powders attain a semi-molten state at 250 °C, showing that nanoscale Ni powders can be sintered easily.

MgO support has a high dispersive effect resulting in high dispersion of NiO. In addition, the interaction of NiO and MgO prevents the dispersion of particles on the support during the thermal treatment. However, some nanoscale NiO particles aggregate to form particles of large sizes, and the others permeate into the MgO resulting in the sintering process as the temperature increases to 800 °C.

Carbon nanofibres were fabricated at 550 °C, 600 °C, 700 °C and 800 °C using the Ni/MgO catalyst precursor sample A obtained by the self-propagating combustion process. Definite amounts of catalyst precursors were introduced into the horizontal ebullition stove [23]. Then the furnace was heated to a set temperature with the flow of H_2 for 30 min and the flow of CH_4 for 60 min, respectively. After being cooled to room temperature in Ar, the carbon nanofibre products were obtained. The yield of carbon nanofibres η may be calculated by the following formula:

$$\eta = \frac{m_{\text{carbon nanofibres}}}{m_{\text{catalyst}}} \times 100 \qquad [\%]$$

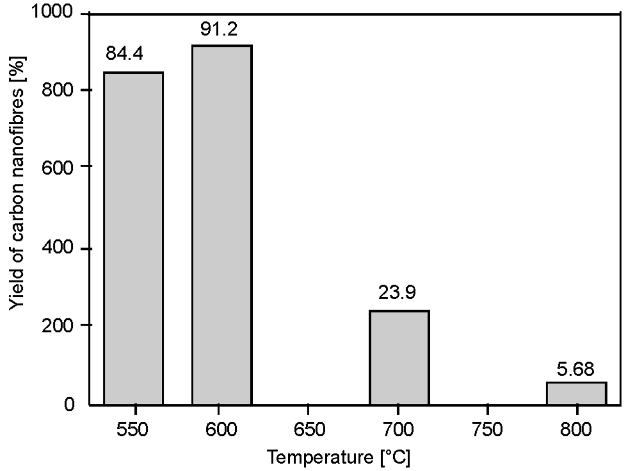

Fig. 6. The yield of carbon nanofibres fabricated with a Ni/MgO catalyst at various temperatures

According to Figure 6, the best growth temperature for the carbon nanofibres is 600 °C, with the highest yield of 91.25%. The yield of the carbon nanofibres decreases dramatically with the temperature, further showing that the temperature plays an important role in the formation of Ni/MgO solid solution. NiO diffuses into MgO, resulting in the formation of the NiO/MgO based solid solution after high temperature roasting at 700 °C and preventing the reduction of NiO. At the same time, Ni/MgO reduced from NiO/MgO at 550~600 °C is the most efficient catalyst for growing the carbon nanofibres.

Ni/MgO catalyst precursors were fabricated using citric acid as the gelling agent. Esterification and dehydration occur in the presence of citric acid under acid conditions, forming a sol-gel skeleton of a high molecular polymer with a complex netted texture, because citric acid belongs to hydroxy acids containing both with –COOH and –OH groups in the molecule. The netted texture provides electron pairs as the Lewis base and metal ions Mg^{2+} and Ni^{2+} provide empty orbitals as the Lewis acids. Complex reaction occurs among metal ions and a high molecular polymer to form carboxylic acid salt dispersing in the gels without segregation of the composition.

Citric acid salt gels formed from nitrate salt and citric acid are characteristic products of self-propagating combustion. Nitrate salt and citric acid are used as the oxidation agent and the reduction agent, respectively. *In-situ* oxidation-reduction reaction occurs between NO_3^- and COO^{2-} of the gels at a specific temperature, resulting in low temperature self-propagating combustion. NiO and MgO powders are formed from metal ions with the exothermic reaction. Then the NiO/MgO solid solution is further formed with the increase in temperature. The chemical reaction becomes complete only when the ratio of oxidation agent to reduction agent is 1:1. Liu et al. [24] analysed the synthesis of NiO with citric acid and $Ni(NO_3)_2$ as the starting materials. According to the propellant thermal chemical theory, the theoretical ratio of the $Ni(NO_3)_2$ to citric acid is 1.8:1 when the total oxidation valence is equal to the total reduction valence. However, unlike the above results, the self-propagating combustion process is most efficient when the ratio of the nitrate salt and citric acid is 1:1 which may be caused by the effect of the O_2 in the air during the self-propagating combustion. The oxidation agent is not sufficient with the increasing content of citric acid resulting in decarbonization of the excessive citrate and the decrease of the combustion zone temperature. The results are confirmed by the weight loss of samples C and D at 350 °C (Fig. 1a). At the same time, the crystal size of NiO/MgO solid solution also decreases obviously with the temperature decrease in the combustion zone.

The combustion temperature for the dry gels originating from the nitrate salt and citric acid is an important factor for the formation of NiO/MgO solid solution. The proportion of the solid solution in the products is essential for the catalyst activity of the Ni/MgO. Two formation process of the solid solution may occur due to the effect of the temperature during the reaction of NiO and MgO:

- Reductive NiO based MgO/NiO solid solution may form with the diffusion of NiO on the surface of MgO (1).
- MgO based NiO/MgO solid solution difficult to reduce also may occur as NiO diffuses into the MgO lattice. Therefore, the catalyst activity of Ni/MgO is determined by the location of NiO in the MgO.

4. Conclusions

Ni/MgO catalysts were prepared using nitrate salt and citric acid at various ratios, by the sol-gel self-propagating, low temperature combustion. Thermal decomposition of the catalyst precursor gels was analyzed in detail. Close attention was given to how the ratio of citrate and nitrate salt influences the particle size of the catalyst precursors, and also the role of temperature on the sintering property of the catalysts is considered. The gels decompose dramatically when the ratio of the nitrate salt to citric acid is 1:1. The particle size of the catalyst precursors decreases in inverse proportion to the citric acid content. The crystalline structures of the catalyst precursors obtained by the self-propagating combustion are the same as those produced by the sintering process. This means that Ni/MgO catalyst precursors can be obtained by the self-propagating combustion but without high temperature sintering. MgO-based NiO/MgO solid solution, which is difficult to reduce, may result from NiO diffusion into the MgO lattice as temperature increases. The results show that the method takes great advantage of simplicity of the apparatus and synthesis process in which the particle size of Ni/MgO can be controlled, making it suitable for syntheses of the catalysts of carbon nanofibres.

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