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Article

Formation mechanism of highly dispersed semi-embedded ruthenium nanoparticles in porous carbon matrix determined by in situ temperature-programmed infrared spectroscopy

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ABSTRACT

The carbonization process of a sucrose-RuCl₃/SBA-15 composite towards a Ru-containing ordered mesoporous carbon (Ru-OMC) catalyst was studied by in situ temperature-programmed infrared spectroscopy to identify the stabilization role of organic carbon precursors during the formation of highly dispersed Ru nanoparticles. The results show that the formation of metal carbonyl species results in the formation of homogeneously distributed Ru nanoparticles, and the rigid silica support and carbon matrix around the Ru(CO)_x complex can significantly avoid the sintering and agglomeration of Ru metal particles during elevated temperature thermal treatment. These results ultimately demonstrate that sucrose plays important roles in the formation of homogeneously distributed Ru nanoparticles in a porous carbon matrix.

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1. Introduction

Metallic nanoparticles (NPs) finely dispersed over carbon supports have been widely used as heterogeneous catalysts, which are important for many industrial applications including the productions of clean fuels, chemicals and pharmaceuticals [1,2]. However, immobilization of highly dispersed metallic nanoparticles on a carbon support remains a challenge since the conventional methods, such as deposition-precipitation and impregnation, are inefficient owing to the inert carbon matrix that shows weak interaction with metallic nanoparticles and therefore cannot anchor tiny particles with a high surface energy [3]. Furthermore, the weak interaction between the inert carbon matrix and metallic nanoparticles always results in sintering and leaching during reaction. Preparation of highly stable carbon-supported metal NPs is still a great challenge,

although enormous efforts have been devoted toward improving the stability of metallic nanoparticles by increasing the number of surface functional groups of the carbon support [4,5]. Therefore, the development of a new methodology to synthesize active and stable carbon-supported metal NPs for wide application in catalysis is highly desirable [6,7].

Unique and unexpected properties have been observed by embedding metal nanoparticles in inorganic pores or matrixes, which indeed offer new opportunities for the design of advanced catalytic systems [8]. An efficient method for the preparation of carbon-confined metal NPs catalysts is the simultaneous introduction of a metal and carbon precursor during the carbon formation process. The early work reported by Liu et al. [9,10] concerned the preparation of the highly dispersed platinum and stable PtRu NPs in ordered mesoporous carbons by dispersing platinum acetylacetonate in furfural alcohol and

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trimethylbenzene as the co-feeding carbon and Pt precursor. Subsequently, Su et al. [11,12] reported that Ru NPs could be semi-embedded in a matrix of porous carbon through a chemical vapor deposition method. Both Xiong et al. [13] and Scholz et al. [14] reported a method of mixing metal precursors and carbon precursors for the preparation of stable metal NPs embedded in the mesoporous carbon material. We also reported a controlled synthesis method of highly dispersed semi-embedded ruthenium nanoparticles in a porous carbon matrix with an increasing number of exposed active sites by using $\text{RuCl}_3/\text{SBA-15}$ as a hard template [15–17]. This Ru-OMC catalyst shows a remarkably high activity and stability in benzene hydrogenation owing to its more exposed Ru surface and semi-embedded status of Ru metal particles. It has been found that the sintering of Ru metal particles is not observed even at temperatures up to 850 °C and most of the Ru metal particles are exposed after the silica templates were removed [15–18]. However, the mechanism for the formation of uniform highly dispersed Ru nanoparticles is still unclear. To understand the mechanism of the stabilization role of carbon precursors during the formation of Ru NPs, in situ IR spectroscopy and temperature programmed thermal treatment experiments were performed and discussed in this work.

As Schlögl recently noted, “catalysts are currently prepared rather than synthesized,” so that the rationally guided syntheses of the desired size, structure and compositionally controlled supported-nanoparticle catalysts are generally lacking [19]. Despite the extensive literature on heterogeneous catalyst preparation, relatively little is known about the mechanism for the formation of the active catalyst. One main reason for this paucity of mechanistic information is the lack of experimental methods able to follow heterogeneous catalyst formation in real time [20]. Fortunately, the recent development of analytical tools to accurately study chemical processes on a molecular scale have provided the opportunity to better understand the mechanisms that govern catalytic reactions and surface science. For instance, in situ techniques have been developed for the investigation of the physicochemical changes of catalysts at a high temperature and pressure [21]. Gates et al. [22–25] investigated the changes in the nuclearity of the essentially molecular surface species as they formed, including the ligands on a noble metal (Ru, Rh, Ir) and the metal-support interactions in real time, by transient infrared spectroscopy and X-ray absorption fine structure spectroscopy. Mondloch and co-workers [20,26] described the development of a kinetic monitoring method for following the kinetics of supported-nanoparticle formation in contact with a solution, and extensive state-of-the-art efforts have also been made to thoroughly characterize the intermediates of catalysts during preparation by transient infrared (IR) spectroscopy and X-ray absorption fine structure spectroscopy.

In the present work, in situ IR spectroscopy combining thermogravimetric and mass spectroscopy techniques was used to investigate the preparation process of an ordered mesoporous ruthenium containing carbon catalyst with uniform metal nanoparticles semi-embedded in a porous carbon matrix. We attempt to explain the interaction between metal

ions and carbon precursors and provide insight into the formation mechanism of highly dispersed semi-embedded ruthenium nanoparticles in porous carbon matrix.

2. Experimental

2.1. Materials

Mesoporous SBA-15 silica was synthesized according to the procedure of Zhao et al. [27]. Typical procedures for preparation of the sucrose- $\text{RuCl}_3/\text{SBA-15}$ composite were as follows: SBA-15 silica (1.0 g) was impregnated with aqueous solution (4.5 mL) containing $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.1 g, Sino-Platinum Metals Co. Ltd). After being dried at 110 °C overnight, $\text{RuCl}_3/\text{SBA-15}$ was obtained. A precursor solution, containing sucrose (1.25 g) and distilled water (2.5 mL) was allowed to infiltrate the mesopores of the $\text{RuCl}_3/\text{SBA-15}$. The sucrose- $\text{RuCl}_3/\text{SBA-15}$ composites were obtained after been dried at room temperature. The Ru-OMC catalyst was synthesized according to our previous report [15,16].

2.2. Characterization

Samples for in situ transmission IR spectroscopy were prepared as self-supported thin films that were pressed using a hydraulic press. In situ transmission IR spectra were recorded by a Nicolet Nexus 470 spectrometer with a quartz cell with both ends “capped” by IR-transparent CaF_2 windows and cooled by flowing water. The cell was wrapped with a heater strip to allow spectra to be collected at elevated temperatures, while the temperature was monitored by a thermocouple placed in close proximity to the catalyst samples. Reference spectra of the clean surfaces in the presence of inert gas were collected. Transmission IR spectra were recorded by a Nicolet Nexus 470 spectrometer equipped with an MCT-A detector cooled by liquid nitrogen with a spectral resolution of 2 cm^{-1} , using a KBr pellet.

Thermogravimetric (TG) measurements for the as-synthesized sucrose- $\text{RuCl}_3/\text{SBA-15}$ composites were performed using a Netzsch thermo balance STA 409. TG profiles were recorded from 50 to 800 °C in flowing helium (75 mL/min) with a linear heating rate of 10 °C/min. The composition of the off-gas was analyzed using an online Pfeiffer Omnistar mass spectrometer.

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images of the samples were obtained by an FEI Tecnai G20 instrument with a field emission gun as the source of electrons operated at 200 kV. Samples were mounted on Quantifoil microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient condition. X-ray photoelectron spectroscopy measurements were conducted on a Kratos AXIS Ultra DLD instruments using 300W Al K_α radiation and C 1s peak at 284.6 eV as the internal standard.

3. Results and discussion

3.1. Role of sucrose on stabilization of Ru NPs during carbonization

Table S1 provides the texture properties, dispersion of Ru and activities of ruthenium-carbon catalysts for benzene hydrogenation. It can be seen that the dispersion of Ru metal nanoparticles of Ru-OMC was higher than that of the Ru/OMC catalysts. The TOF for Ru-OMC catalyst reached 9.75 s^{-1} , which was approximately 12 times higher than that of the OMC-supported Ru catalyst (Ru/OMC) with a similar Ru loading. This may arise from the higher dispersion of Ru nanoparticles prepared by the present sucrose stabilized approach and the highly intimate contact between the Ru nanoparticles and the carbon support [15,16]. Detailed characterizations and the catalytic performance of OMC-supported Ru catalysts and Ru-OMC catalysts have been reported in our previously published papers [15,16]. Highly dispersed Ru nanoparticles with sizes of 1–2 nm were uniformly distributed within the support and no particle aggregation was observed for Ru-OMC (Fig. 1 (a)). No particle aggregation was observed even after continuous reaction for 24 h at 150°C (Fig. 1(b)). Fig. 1(c) and (d) show the TEM images for the Pt-OMC and Ni-OMC catalysts. It could be observed that highly dispersed Pt nanoparticles with sizes of 3–5 nm were uniformly distributed within the carbon substrate, and no particle aggregation was observed. However, in contrast to Ru and Pt, the particles on Ni-OMC were not as homogeneous as the above samples. Only large particles (>30 nm) could be observed, as shown in Fig. 1(d). In this paper, only the mechanism for the formation of Ru nanoparticles was investigated.

In the present one-pot synthesis approach, the RuCl_3 was first introduced in the pores of the SBA-15 templates. Sucrose was then introduced after the metal precursors (Scheme 1). Then, the solvent was volatilized and the sucrose cross-linked and polymerized, which was initiated by thermal treatment. The composite was carbonized at 850°C for 3 h under nitrogen flow. The Ru-OMC catalyst was obtained after etching the template. As reported in the aforementioned results and in our previous reports [15,16], the method which uses sucrose as carbon precursor was suitable for the preparation of metal containing carbon catalysts with homogeneously distributed nanoparticles. Coincidentally, Scholz et al. [14,28] also mentioned that polymerized furfuryl alcohol was able to protect the

Fig. 1. TEM images for fresh (a) and used (b) Ru-OMC, Pt-OMC (c) and Ni-OMC (d) catalysts.

PtRu nanoparticles from agglomeration during high temperature carbonization. However, there was still no direct evidence to demonstrate the interaction between the metal ion and carbon precursor. In the present one-pot facile synthesis approach, the nucleation and stability of Ru nanoparticles were highly dependent on the interaction between the carbon precursors and Ru ion. Therefore, it is meaningful to monitor the interaction between carbon precursors and Ru ion in situ during the carbonization process.

3.2. Interaction between Ru^{3+} and carbon precursor during carbonization

Before the study of the carbonization process by in situ spectroscopy, the FT-IR spectra of SBA-15, $\text{RuCl}_3/\text{SBA-15}$, sucrose, sucrose/SBA-15 and sucrose- $\text{RuCl}_3/\text{SBA-15}$ were measured and are given in Fig. 2. As shown in Fig 2(a), the characteristic bands for silica were present for calcined SBA-15. The bands at $765\text{--}862$ and $995\text{--}1310 \text{ cm}^{-1}$ were assigned to Si-O bending and stretching vibrations, respectively. The band at $865\text{--}995 \text{ cm}^{-1}$ was assigned to the SiO-H rocking vibration. The

Scheme 1. Schematic illustration of the synthesis of Ru-OMC with uniformly semi-embedded Ru NPs by a one-pot approach from a sucrose- $\text{RuCl}_3/\text{SBA-15}$ composite and normal impregnation approach for Ru/OMC.

Fig. 2. FT-IR spectra of SBA-15 (a), $\text{RuCl}_3/\text{SBA-15}$ (b), sucrose (c), sucrose/SBA-15 (d), sucrose- $\text{RuCl}_3/\text{SBA-15}$ (e) at room temperature and sucrose- $\text{RuCl}_3/\text{SBA-15}$ (f) after thermal treatment at 350 °C for 3 h in an argon flow.

broad absorption band from 3764 down to 2702 cm^{-1} was assigned to the SiO–H stretching vibration. The strong absorption band at 1555–1768 cm^{-1} was attributed to the bending vibration of both free H_2O and H_2O which is hydrogen-bonded to the proton of the silanol groups [29]. The characteristic band of $\text{RuCl}_3/\text{SBA-15}$ was similar to that of SBA-15, as shown in Fig 2(b), which indicated only a physical adsorption behavior occurred after impregnation of RuCl_3 on the SBA-15 support. It may also be that the interaction of RuCl_3 with silica was too weak to be observed owing to the low loading of RuCl_3 . Fig. 2(c) shows the spectrum of sucrose. The absorption bands at 1134, 1048, 992 and 924 cm^{-1} were characteristic of sucrose, which result from C–O and C–C stretching vibrations [30]. The band at 979 cm^{-1} was assigned to the stretching vibrations C–C in the ring while the band at 1034 cm^{-1} was associated to the C–O stretching vibration of the $\text{CH}_2\text{--OH}$ group, since the other C–O stretching in the ring was expected to contribute at higher wavenumbers. For the sucrose/SBA-15 composite (Fig. 2(d)), the spectrum showed characteristic bands of both sucrose and SBA-15 silica. However, the characteristic band of O–H at 3560 cm^{-1} disappeared and the intensity of C–H bands at 2941 cm^{-1} decreased compared with the spectrum of sucrose, which suggested a weak interaction between sucrose and SBA-15 silica. Fig. 2(e) shows the spectrum of sucrose- $\text{RuCl}_3/\text{SBA-15}$. The spectrum was similar to the spectrum of sucrose/SBA-15. This indicated that the existence of RuCl_3 did not affect the sucrose-silica interaction, or alternatively, the effect was too weak to be observed by IR spectroscopy.

To probe the interaction between a metal ion and carbon precursor during the carbonization steps, a series of temperature programmed in situ IR spectroscopy experiments were performed on the sucrose- $\text{RuCl}_3/\text{SBA-15}$ composite. The same

experiments were performed on $\text{RuCl}_3/\text{SBA-15}$ and sucrose/SBA-15 as blank experiments to identify the interaction of Ru^{3+} and sucrose. Fig. 2(f) shows the total FT-IR spectrum of sucrose- $\text{RuCl}_3/\text{SBA-15}$ carbonized at 350 °C for 3 h in the range of 1000–4000 cm^{-1} . Four sharp peaks appeared at 1610, 1723, 1968 and 2048 cm^{-1} after thermal treatment. The band at 1610 cm^{-1} corresponded to C=C groups, which revealed the aromatization of the samples [31], and the band at 1723 cm^{-1} was assigned to C=O stretching vibrations corresponding to the carbonyl, quinone, ester or carboxyl groups [32]. As reported in the literature, the peaks in the range of 1900–2100 cm^{-1} could be assigned to the C=O stretching vibrations which were coordinated with transition metal [33]. Therefore, the sharp peaks at 1968 and 2048 cm^{-1} were most likely derived from the interaction between Ru^{3+} and the carbon precursor (sucrose). The absorption band at 2938 cm^{-1} increased after thermal treatment, which was assigned to C–H stretching vibrations corresponding to methylene of carbonized sucrose. The temperature programmed in situ IR spectra of sucrose- $\text{RuCl}_3/\text{SBA-15}$ recorded in the range of 1500–2200 cm^{-1} under different temperatures are shown in Fig. 3(a). The spectra were taken every 50 °C from room temperature to 500 °C. Two new bands around 1991 and 2064 cm^{-1} clearly appeared and their intensities increased when the temperatures were further increased. When the temperature reached 350 °C, the intensity of the two bands around 1991 and 2064 cm^{-1} was maximized. The intensity of the bands around 1991 and 2064 cm^{-1} decreased significantly as the temperature was further increased from 350 to 500 °C. Meanwhile, the aromatic C=C stretching band at 1610 cm^{-1} increased and broadened, which suggested that the aromatic rings existing originally as highly substituted or cross-linked states were converted to simple

Fig. 3. In situ FT-IR spectra of sucrose-RuCl₃/SBA-15 (a), sucrose/SBA-15 (b), RuCl₃/SBA-15 (c) and sucrose-Ru⁰/SBA-15 (d) during thermal treatment at different temperatures in an argon flow.

aromatics by pyrolysis [34,35].

To ensure that the bands at 1990–2100 cm⁻¹ were derived from the interaction between Ru³⁺ and carbon precursor (sucrose), the in situ FT-IR spectra of sucrose/SBA-15 and RuCl₃/SBA-15 during thermal treatment as a function of temperature under inert gas were measured and are shown in Fig. 3(b) and (c). There were only bands at 1605 cm⁻¹ corresponding to aromatic C=C groups and the bands at 1723 cm⁻¹ corresponding to the C=O stretching for sucrose/SBA-15. It could be seen that there were no apparent peaks in the range of 1990–2100 cm⁻¹ for sucrose/SBA-15 and RuCl₃/SBA-15, except for the characteristic absorption bands associated with SiO₂ and carbonized sucrose. Therefore, it could be inferred that the bands at 1990–2100 cm⁻¹ were derived from the interaction between Ru³⁺ and sucrose during thermal treatment. The in situ FT-IR spectra of the reduced Ru⁰/SBA-15 impregnated

with a sucrose sample (Sucrose-Ru⁰/SBA-15) thermally treated in an argon flow was also obtained and the data are shown in Fig. 3(d). It can be seen that the spectra of this sample at different temperatures were totally different from those of the sucrose-RuCl₃/SBA-15. There was no apparent peak in the range of 1990–2100 cm⁻¹ observed for sucrose-Ru⁰/SBA-15, except for the characteristic absorption bands associated with SiO₂ and carbonized sucrose. This result indicated that the characteristic absorption bands in the range of 1990–2100 cm⁻¹ were not caused by the CO released during the carbonization of sucrose adsorbing on the pre-reduced Ru metal site. Therefore, it could be inferred that the bands at 1990–2100 cm⁻¹ were derived from the interaction between Ru³⁺ and sucrose during thermal treatment.

The sucrose-RuCl₃/SBA-15 composite was submitted for TG analysis to determine the chemical change and weight loss of

Fig. 4. TG and DTG profiles of sucrose-RuCl₃/SBA-15 in an argon flow and the corresponding mass spectra analysis for $m/e = 15, 18, 28, 29$ and 44 .

the sucrose-RuCl₃/SBA-15 composite during carbonization, and the gas products released were analyzed by mass spectroscopy. The TG and DTG profiles of sucrose-RuCl₃/SBA-15 in the presence of inert gas as well as the corresponding mass spectra analysis for $m/e = 15, 18, 28, 29$ and 44 are presented in Fig. 4.

First, a cumulative weight loss of approximately 8% was observed between 50 and 150 °C. As $m/e = 18$ was detected, this indicated a dehydration of the composite materials may have occurred in this temperature range. Second, a weight loss of approximately 35% was observed between 150 and 500 °C, and mass numbers of 15, 18, 29 and 44 were detected. While $m/e = 18$ could be assigned to water; $m/e = 15, 29$ and 44 could be related to carbonaceous decomposition products in the forms of CH₃, CHO fragments and CO₂, respectively. The above results indicated that several processes, such as dehydration, decarbonylation, and pyrolysis of the organic matrix, occurred simultaneously in this temperature range [36], which lead to the formation of amorphous carbon. Furthermore, $m/e = 35$ could be attributed to the desorption of chlorine resulting from the decomposition of RuCl₃· x H₂O (Fig. S3). When the temperature was increased to 800 °C, a weight loss of approximately 4%, which was assigned to the shrinking of the amorphous carbon matrix and dehydration of the surface oxygen-containing groups like carbonyl and carboxyl [16], could be observed. This illustrated that the main amorphous carbon matrix was formed before 500 °C.

3.3. Carbonization process of sucrose-PtCl₆²⁻/SBA-15 and sucrose-Ni²⁺/SBA-15

To determine if the interaction between Ru³⁺ and sucrose during carbonization was exclusive for the synthesis of metal nanoparticles embedded in a carbon substrate, the in situ IR spectroscopy was also applied for the study of the carbonization process for a composite of sucrose-H₂PtCl₆/SBA-15 and sucrose-NiCl₂/SBA-15 under the same conditions. Pt and Ni catalysts are generally used as hydrogenation catalysts [9,10,37]. Fig. 5(a) shows the change of the in situ IR spectra of

Fig. 5. In situ FT-IR spectra of sucrose-HPt₂Cl₆/SBA-15 (a) and sucrose-NiCl₂/SBA-15 (b) during thermal treatment at different temperatures in an argon flow.

sucrose- $\text{H}_2\text{PtCl}_6/\text{SBA-15}$ recorded in the range of 1500–2200 cm^{-1} with increasing temperatures. Similar to what was observed with the sucrose- $\text{RuCl}_3/\text{SBA-15}$ composite, two bands around 2043 and 2105 cm^{-1} were observed when the temperature was increased to 160 °C which may be attributed to the interaction between PtCl_6^{2-} and sucrose during carbonization. However, the intensities of the bands were obviously weaker than that observed for sucrose- $\text{RuCl}_3/\text{SBA-15}$, which may be related to the properties of the metals.

However, there is no appearance of the bands at the region of 1900–2100 cm^{-1} during the carbonization of sucrose- $\text{NiCl}_2/\text{SBA-15}$, except for the characteristic absorption bands associated to SiO_2 and carbonized sucrose, as shown in Fig. 5(b). A larger particle may form just as the particle nucleation, although the strong confinement effect of carbon structure can restrain the sintering of nickel particles. The reason may be that a larger particle was formed just as the particle became nucleated, although the strong confinement effect of the carbon structure could restrain the sintering of nickel particles. Therefore, it was illustrated that the formation of a metal-carbonyl complex is of benefit for the formation of homogeneous small nanoparticles.

X-ray photoelectron spectroscopy was used to characterize the status of RuCl_3 in sucrose- $\text{RuCl}_3/\text{SBA-15}$ carbonized at different temperatures, since the $\text{Ru } 3d$ signals were overlapped with the $\text{C } 1s$ signal in the XPS studies. The $\text{Ru } 3p$ XPS spectra are given in Fig. 6. It shows that the $\text{Ru } 3p_{3/2}$ peak for sucrose- $\text{RuCl}_3/\text{SBA-15-160 } ^\circ\text{C}$ was centered at 463.8 eV, which could be assigned to the cationic Ru^{3+} species. This indicated that the ruthenium species were still in a cationic state when the composition was thermally treated at 160 °C. It should be mentioned that the binding energy of Ru^{3+} for the sucrose-ruthenium/SBA-15 composite prepared at 160 °C was higher than that of Ru^{3+} in RuCl_3 (463.3 eV), which suggested that an interaction occurred between Ru^{3+} and the hydroxyl in sucrose. The $\text{Ru } 3p_{3/2}$ peak for sucrose- $\text{RuCl}_3/\text{SBA-15-350 } ^\circ\text{C}$ was shifted to 462.3 eV. This shift of the binding energy indicated that the Ru ions were gradually reduced into a reduction state. However, this binding energy was still higher than the

Fig. 6. $\text{Ru } 3p$ XPS spectra of the sucrose- $\text{RuCl}_3/\text{SBA-15}$ composite prepared with different carbonization temperatures of 160 (1), 350 (2) and 850 (3) °C.

position of the metallic Ru^0 species reported previously (461.1–461.6 eV) [7]. There was almost a 0.7–1.2 eV shift of the binding energy. This shift could be caused by the electrons transferring from the surface oxygen functional groups, such as carboxyl groups, to the Ru orbitals. This suggested that coordination bonds were formed between the Ru^0 and CO groups at the surface of the carbon materials during the carbonization process. The $\text{Ru } 3d$ and $\text{C } 1s$ spectra of the above samples are provided in Fig. S6. The shift phenomenon of the Ru peaks in $\text{Ru } 3d$ spectra was similar with that in the above analysis.

3.4. Discussion

In the present work, at first, Ru ions were uniformly adsorbed on the surface of the mesopore walls of SBA-15. By incorporating sucrose into $\text{RuCl}_3/\text{SBA-15}$, the Ru ion was surrounded by sucrose with abundant hydroxyl groups. The abundant hydroxyls of sucrose provided a strong interaction with Ru ions. The Ru ions were gradually reduced to Ru^0 at 200–350 °C, which was proved by XPS in our previously published paper and Fig. 6 [15]. Meanwhile, the hydroxyl groups of sucrose were dehydrated into carbonyl and coordinated with Ru^0 , which was demonstrated in Fig. 3(a). A similar phenomenon has been reported by Zhang et al. [38], where the noble metal precursors can be reduced by an abundance of hydroxyl groups in polymers such like poly-(ethylene glycol) (PEG) and poly-(ethylene oxide) (PEO) at approximately 100 °C.

The formation of a metal-carbonyl complex was observed during carbonization in the temperature range of 200–500 °C. However, the results obtained from the spectra of C=O were much more complicated because of the presence of several different C=O species on different types of reduced and partially oxidized Ru sites, which made the interpretation of the observed spectra more difficult than with other metals [39–41]. Fig. 7(a) shows the FT-IR spectra of triruthenium dodecacarbonyl. Four sharp peaks appeared at 1985, 1997, 2022 and 2059 cm^{-1} . The bands at 1985 and 1997 cm^{-1} were ascribed to equatorial carbonyls, while the bands at 2022 and 2059 cm^{-1} were ascribed to the axial carbonyls [42,43]. Figure 7b shows the FT-IR spectra of CO adsorbed on $\text{Ru}^0/\text{SBA-15}$. The band at 2023 cm^{-1} was ascribed to the CO linearly adsorbed on Ru^{n+} with a low coverage, while the bands at 2078 and 2135 cm^{-1} represented vibrations of $\text{Ru}^{n+}(\text{CO})_x$ multicarbonyls [44,45]. By comparing the FT-IR spectra of sucrose- $\text{RuCl}_3/\text{SBA-15}$ during thermal treatment with those of CO adsorbed on $\text{Ru}^0/\text{SBA-15}$ and triruthenium dodecacarbonyl, it was supposed that the interactions between the Ru species and carbon precursors were different from those of CO adsorbed on $\text{Ru}^0/\text{SBA-15}$ and triruthenium dodecacarbonyl. Meanwhile, the decomposition temperature of triruthenium dodecacarbonyl is 170 °C (Fig. S5). However, the $\text{Ru}(\text{CO})_x$ complex confined in the carbon-silica composite was stable until the temperature was increased to 500 °C.

Although classifying the complicated species was difficult owing to the presence of several different C=O species on different types of Ru sites, there was no doubt that the Ru species

Fig. 7. FT-IR spectra of triruthenium dodecacarbonyl (a) and adsorption of CO on Ru⁰/SBA-15(b).

exhibited a strong interaction with the carbon precursor. The gradual decomposition process of the bonds between the surface atoms and C=O ligands appeared to determine the rate of formation of the final metallic state of the nanoclusters [22,46]. In the present one-pot facile synthesis approach, following the degradation of the Ru(CO)_x complex, the metal species were involved in the nucleation and growth process while the main carbon matrix had already formed, which provided a strong confinement effect. The Ru(CO)_x complex degraded gradually resulted in low local ad-atom concentrations on the support surface, which restrained the growth of large crystallites. Additionally, the strong confinement effect of the carbon matrix impeded crystallite migration, which involved the mobility of particles in a Brownian-like motion on the support surface with the subsequent coalescence leading to growth of the nanoparticles [47,48]. Therefore, the rigid silica support and carbon matrix around the Ru(CO)_x complex could significantly avoid the sintering and agglomeration of Ru metal particles during high temperature thermal treatment. Meanwhile, optimization of the Ru-OMC catalysts could be performed at the level of the molecularly well-defined homogeneous precursor before conversion into the ultimate active catalysts. According to this synthesis approach, ultimately, the formation and size of the Ru metal particles could be controlled by the surrounding sucrose. A similar phenomenon has been reported from a study involving the cooperative assembly of a β-cyclodextrin host-guest complex and ruthenium trichloride through non-covalent interactions [49].

Fig. 8 shows the TEM images of the sucrose-RuCl₃/SBA-15 composite prepared with different carbonization temperatures. The Ru nanoparticles were not observed in the sucrose-RuCl₃/SBA-15 composite carbonized at 160 °C, as shown in Fig. 8(a) and (b). It was reasonable that the Ru³⁺ could not be reduced at such a low temperature. However, it was observed that the Ru nanoparticles were embedded in the carbon-silica

composite after being carbonized at 350 °C (Fig. 8(c) and (d)), which demonstrated Ru nanoparticles had formed. Similarly, Fig. 8(e) and (f) shows that the Ru nanoparticles were embed-

Fig. 8. TEM images of sucrose-ruthenium/SBA-15 composite prepared with different carbonization temperature. 160 (a, b), 350 (c, d), 500 (e, f) °C.

ded in the carbon-silica composite without aggregation after being carbonized at 500 °C.

4. Conclusions

The preparation processes of ordered mesoporous metal containing carbon catalysts have been investigated by in situ IR spectroscopy. The results demonstrate that Ru species has a strong interaction with carbon precursor in the preparation process of an ordered mesoporous ruthenium containing carbon catalyst, particularly during the carbonization. XPS of the intermediates during carbonization shows that the Ru ions were gradually reduced to Ru⁰ by the abundant hydroxyl groups of sucrose at 200–350 °C. The formation of a metal-carbonyl complex, which affects the nucleation and growth of metal nanoparticles, is beneficial for the formation of homogeneous small nanoparticles and the subsequent strong confinement effect of the carbon structure restrains the growth of the metal nanoparticles at elevated temperature. It is interesting to note that an interaction is observed between Pt and sucrose during the carbonization but is not observed between Ni and sucrose. Finally, the understanding of the preparation processes for metal-incorporated mesoporous carbons could contribute to the design of new robust carbon-supported noble metal catalysts with high metal dispersions and stability.

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Graphical Abstract

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Formation mechanism of highly dispersed semi-embedded ruthenium nanoparticles in porous carbon matrix determined by in situ temperature-programmed infrared spectroscopy

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In situ spectroscopy was applied to the carbonization of a sucrose-RuCl₃/SBA-15 composite towards a Ru-containing ordered mesoporous carbon catalyst to identify the stabilization role of organic carbon precursors during the formation of highly dispersed Ru nanoparticles.

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原位红外光谱法研究中孔炭限域钌纳米催化剂的形成机理

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摘要: 炭载金属纳米催化剂广泛应用于精细化学品加氢反应及燃料电池等许多领域。炭载体因具有较高的表面积、易于调控的表面化学官能团以及特有的耐酸耐碱等性质而经常用作负载型金属催化剂的载体。但是相对于氧化物载体, 炭载体表面较为惰性, 与金属纳米粒子的相互作用较弱, 采用后引入金属前体, 如沉淀-沉积法和浸渍法等方法制备的催化剂, 在液相和高温反应条件下, 金属纳米粒子易流失和烧结。因此制备高稳定性的炭负载金属纳米催化剂仍是多相催化剂制备领域的一个重要课题。随着新型炭材料的出现及纳米孔材料制备科学的发展, 极大丰富和推动了炭载金属催化剂制备方法的发展。近年来, 通过炭热还原法即在制备中孔炭的过程中引入金属前体, 一步制备炭载金属催化剂已经成为炭载金属催化剂的一个新的制备方法。此法制备的催化剂通常具有金属纳米粒子分散均匀、炭和金属活性中心之间的作用力强、热稳定性好、炭载体对负载金属纳米粒子具有限域作用等诸多优点, 而且在诸多催化反应中具有优异的催化性能。例如本课题组曾以RuCl₃/SBA-15为硬模板, 采用原位碳热还原法制备了Ru-OMC催化剂, 它在液相苯环加氢、合成氨及费托合成反应中均具有优异的催化性能及稳定性, 但是对于中孔炭中均匀分散的钌纳米颗粒形成的机理尚不清楚。

基于此, 本文采用原位的红外光谱结合热重表征技术对sucrose-RuCl₃/SBA-15炭化过程钌物种的形成过程及机理进行了研究, 探讨了蔗糖在炭化过程中对高分散钌纳米颗粒形成过程的稳定机制。研究发现, 尽管经历了高达850 °C的高温炭热处理, 所得Ru-OMC催化剂中钌纳米粒子仍然可以均匀分散, 钌粒径在1–2 nm之间。同时, 由于这种方法中钌前体预先负载在SBA-15载体表面, 在炭化过程中, 钌纳米粒子可以均匀地分散在模板氧化硅和形成的炭骨架之间的界面上, 去除氧化硅模板后, 钌纳米粒子可以更多的暴露在中孔炭的孔道内侧, 因而具备更好的催化性能。通过对sucrose-RuCl₃/SBA-15炭化过程中原位红外光谱表征发现, Ru³⁺在炭化过程中逐步被还原, 并和具有含氧官能团的炭前体形成类金属羰基配合物Ru(CO)_x。这种配合物的生成可以有效抑制钌纳米粒子在热处理过程的迁移乃至长大, 因而对得到均匀分散的钌纳米粒子具有至关重要的作用。同时Ru(CO)_x周围刚性的氧化硅模板和碳骨架可以有效地防止钌纳米粒子在高温处理过程中烧结。

和团聚. 对sucrose-RuCl₃/SBA-15炭化中间体的X射线光电子能谱表征进一步证明了Ru³⁺在350 °C之前即可被还原, 钌的3*p*轨道结合能发生了位移, 说明钌和炭载体之间具有较强的相互作用. 该结果可为炭载贵金属催化剂的调控制备及高活性纳米催化剂的形成机理研究提供一定的参考.

关键词: 钌纳米粒子; 红外光谱; 原位; 镶嵌式钌炭催化剂, 中孔炭

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