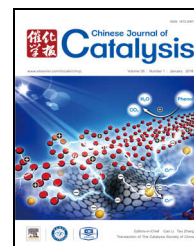


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Article

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

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