DOI: 10.1002/adsc.200700578

Synthesis of Rhodium Colloidal Nano-Coating Grafted Mesoporous Silica Composite and its Application as Efficient Environmentally Benign Catalyst for Heck-Type Reaction of Arylboronic Acids

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Received: December 9, 2007; Published online: March 7, 2008

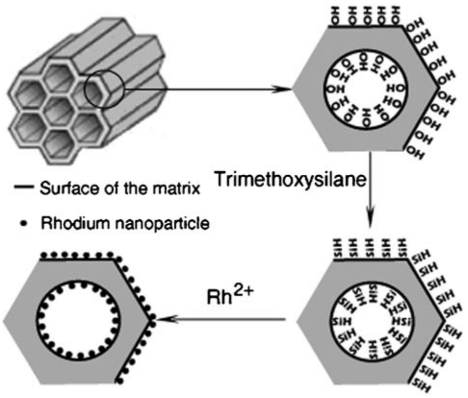
Abstract: The synthesis and characterization of rhodium colloidal layer grafted mesoporous SBA-15 material, designated as SBA-Rh, are presented. In the preparation of this new catalyst, SBA-15 mesoporous material was used as support without any pretreatment. The Si–H functional groups were introduced onto the surface which resulted in highly dispersed metal colloid layer both on the outer and inner surface of the supporting material. The material was investigated for Heck-type coupling reactions of alkenes with ayboronic in organic/water solvent. The ultrahigh specific area, large pore opening, and highly dispersed catalyst species in SBA-Rh material created one of the most active heterogeneous catalysts for such reactions. Rhodium element was not detected in the final mixture by ICP after reaction. The catalyst species showed very high stability against leaching from the matrix and can be recycled for repeated use.

Keywords: C–C coupling; heterogeneous catalysis; mesoporous materials; rhodium

The formation of carbon-carbon bonds lies at the heart of organic chemistry, and the ability to synthesize new and interesting organic molecules is inextricably linked to the discovery of new methods that achieve this objective. In this area, transition metal catalysts, especially the palladium and its compounds, have been extensively employed as instruments for this purpose, which enable the cross-coupling of substrates in ways that would have previously been thought impossible.[1–6] Nowadays, the application of these catalysts has become a cornerstone in the efficient construction of complex organic molecules.

In the past few years, there has been a renewed focus on rhodium catalysts for carbon-carbon forming reactions.[7,8] In addition to showing new and complementary reactivity to other catalyst systems, rhodium catalysis may permit the development of more environmentally benign processes. This is because the reactions can frequently be performed in the presence of water or even in water as the exclusive solvent.[7] Mori reported a rhodium complex-catalyzed carbon-carbon bond formation reaction of silanediols with α,β-unsaturated carbonyl compounds. Heck-type products were obtained in anhydrous solvents, whereas in aqueous solvents, the Michael-type adducts were formed.[9] Zou et al. reported the rhodium-catalyzed Heck-type reaction of arylboronic acids with α,β-unsaturated esters in a water-toluene biphasic medium.[10] All the protocols reported so far for the Heck-type coupling of alkenes with arylboronic acids by rhodium are homogeneous in nature and require an ancillary phosphine ligand. The major drawback of homogeneous catalysis is the need to separate the relatively expensive catalyst from the reaction mixture at the end of the process. Just recently, Rajiv et al. found that the metal rhodium also can catalyze this type of reaction.[11] It can be expected that synthesizing supported, highly dispersed Rh nanoparticles with highly specific surface area will be beneficial to obtain more efficient catalysts.

Mesoporous silica material as a common support for the catalyst has been attracted considerable attention in the past decade due to its excellent thermal and chemical stability. Its large surface area and well-defined tunable nanosized porosity provides a good opportunity for confining the growth of guest materi-



Scheme 1. Schematic illustration of synthetic pathways for rhodium colloidal nano-coating grafted mesoporous silica materials.

als.[12] Besides this, an *in-situ* reduction method for the controlled deposition of metals onto the inner surface of silica mesoporous materials has been disclosed recently by our group.[13] It was shown that the immobilized Si−H group on the pore channel surface is able to *in-situ* reducing metal ions resulting in the formation of a uniform thin metal colloid layer. However, this method is still somewhat complicated. Before immobilization of the Si−H group into the pore channel, the outer surface of the matrix needs to be pre-modified with $-CH_3$ groups and the surfactant in the pore channel needs to be removed by solvent extraction.

In this work, we report the synthesis and characterization of rhodium colloidal nano-coating grafted mesoporous silica materials through a modified *in-situ* reduction method (Scheme 1). Mesoporous silica material SBA-15 was directly used as support without any modification. The metal colloid was evenly dispersed on both the outer and inner surfaces of the matrix. As far as we know, this kind of Rh metal colloidal coating catalyst grafted on mesoporous matrix has not been reported before. The experimental results show that the synthesized composite catalysis materials have high catalytic activity in Heck-type reaction of alkenes with arylboronic acids.

Trimethoxysilane can *in-situ* reduce noble metal ions into metals to form colloidal layers in the channels of mesoporous materials, which had been proved in our previous studies.[13] In that case, in order to prevent the leaching of the catalytic species during the catalytic process, before being functionalized with trimethoxysilane, the outer surface of mesoporous material was first modified with $-CH_3$ groups to ensure the metal colloidal was fabricated only on the pore channel surface of the matrix. Our experiments in this report show that the existence of metal colloids on the outer surface would not lead to leaching of the catalytic species from the mesoporous matrix during the catalytic process. As a matter of fact, the presence of metal colloid on the outer surface prepared without the pretreatment with $-CH_3$ groups can bring many benefits to the catalytic system, such as making the fabrication of the catalyst easier, increasing the contact area between catalyst and reactant, etc., as will be described later.

The FT-IR data shown in Figure 1 present the immobilization process of trimethoxysilane on the surface of masoporous SBA-15. A signal at around 960 cm^{-1}, which can be assigned to the Si−O stretching of the Si−OH groups, was observed in the spectrum of SBA-15. When treated with trimethoxysilane, two new signals at about 2240 and 880 cm^{-1} (due to Si−H stretching and bending vibrations, respectively) appeared, accompanied by a decreased IR absorption of silanol groups at 960 cm^{-1}. This proves that a reaction between $(CH_3O)_3SiH$ and the SiOH groups had occurred, resulting in the creation of Si−H on the surface of the mesoporous material SBA-15.

Figure 2 shows the nitrogen adsorption/desorption isotherms of SBA-15, SBA-H and SBA-Rh and the

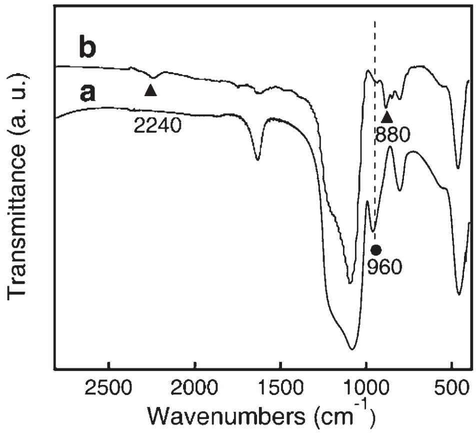


Figure 1. FT-IR spectra for samples of a) SBA-15 and b) SBA-H.

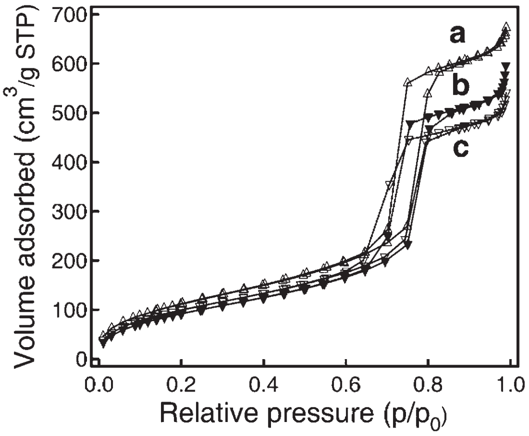


Figure 2. N_2 adsorption-desorption isotherms for samples of a) SBA-15, b) SBA-H and c) SBA-Rh.

Table 1. Pore structure parameters of (a) SBA-15, (b) SBA-H, (c) SBA-Rh.

Sample	A_{BET} [m^2g]$^{-1}$	V_{BJH} [m^3g]$^{-1}$	D_{BJH} [nm]	d_{100} [nm]	A_0 [nm]	Thickness of pore wall [nm]
SBA-15	431	1.10	8.11	9.93	11.47	3.36
SBA-H	380	0.99	7.83	9.93	11.47	3.64
SBA-Rh	353	0.89	6.85	9.93	11.47	4.62

A_{BET}: BET surface area; V_{BJH}: BJH pore volume; D_{BJH}: BJH pore diameter; d_{100}: plane separation; $A_0=(2/\sqrt{3})\cdot d_{100}$.

relative pore structure parameters are summarized in Table 1. Type IV isotherm curves with a well-defined step clearly indicate that these materials possess a mesoporous structure. The decreases of the BET surface area, BJH pore volume and average pore size together with the increased thickness of the pore walls, can be attributed to the incorporation of Rh nanoparticles on SBA-15. However, it can also be seen from Table 1, as compared to the literature, that the BET surface area and the BJH pore volume only have very limited decreases after Rh incorporation (BET surface area decreased from 380 (SBA-H) to 353 m^2g^{-1} (SBA-Rh) and BJH pore volume from 0.99 to 0.89 cm^3g^{-1}, respectively). This suggests that the incorporated rhodium occupied a very limited space and that almost all of the nanopore channels of the host silica remain open. This result is quite different from the previous report where metal nanowires formed and occupied most of the pore space.[15] For some applications, especially for catalysis, the space is important for guest molecules to diffuse into the host silica, and to access catalyst nanoparticles for reactions to be catalyzed.

The as-synthesized SBA-Rh catalyst retained its hexagonally packed porous structure as shown in the small angle XRD pattern (Figure 3), one major peak at about 0.98° (2θ) together with two additional peaks can be observed, which is the characteristic of the hexagonal mesoporous structure of SBA-15. Different from the other reports, in which the peak intensities usually decrease after guest loading, comparatively, the densities in this case only have a slight increase after Rh incorporation, especially for (100) reflections. This is probably due to the relatively high scattering contrasts between the pores and walls resulting from the deposition of uniform Rh colloidal layers in the channels of the host. Rhodium metal has major diffraction peaks at $2\theta=41.0$ (111) and 47.78 (200), which were not found in the XRD pattern of SBA-Rh (Figure 4, Rh content: 5.1 wt%), indicating that rhodium was highly dispersed in a colloidal form. These phenomena have also been observed in our previous studies.[13]

TEM investigation provides the direct observation of the morphology and distribution of rhodium nanoparticles in SBA-Rh. Figure 5, a and b, show the HR-TEM images of a sample of SBA-Rh with the electron beam parallel and perpendicular to the pore channels, respectively. In agreement with the above SAXRD results, the mesoporous channels are well ordered with a characteristic hexagonal structure, as suggested by the electron diffraction patterns. Although some rhodium ions were reduced on the outer surface of the matrix, no bulk aggregation of the metal could be found. On the other hand, pore channels are still open and no nanowires formed in the pore channels. The distribution of the metal colloids is uniform not only on the inner surface but also on the outer surface. The existence of the Rh colloids can be further proved by energy dispersive spectros-

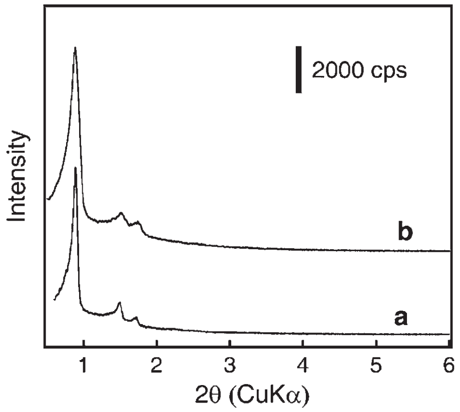


Figure 3. Small angle X-ray diffraction patterns of samples a) SBA-H and b) SBA-Rh.;

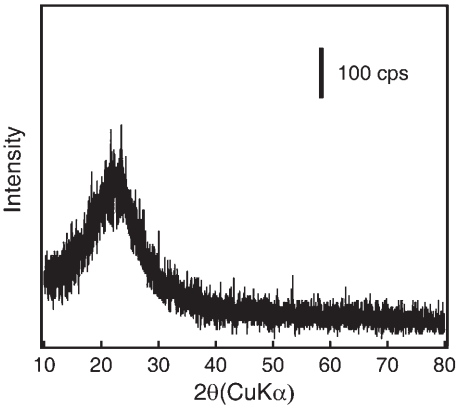


Figure 4. Wide-angle XRD pattern of sample SBA-Rh.

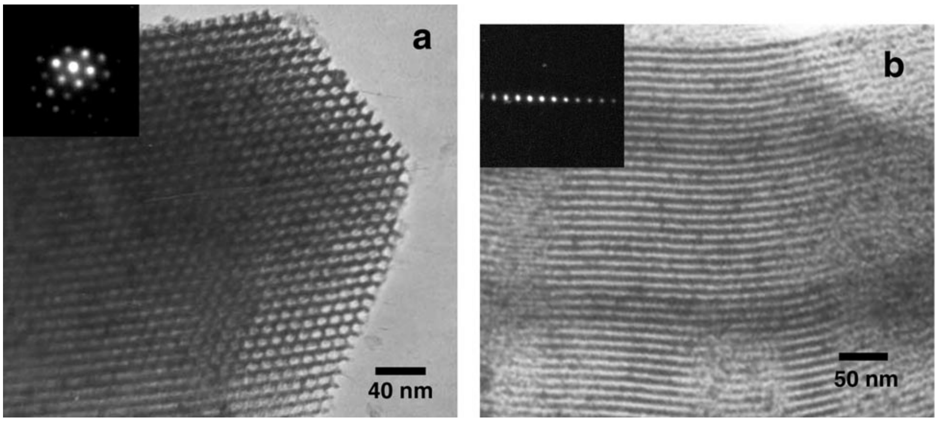


Figure 5. HR-TEM images of SBA-Rh sample and their selected-area diffraction patterns (insets) with (*left*) electron beam perpendicular to pore channels and (*right*) electron beam parallel to the pore channels.

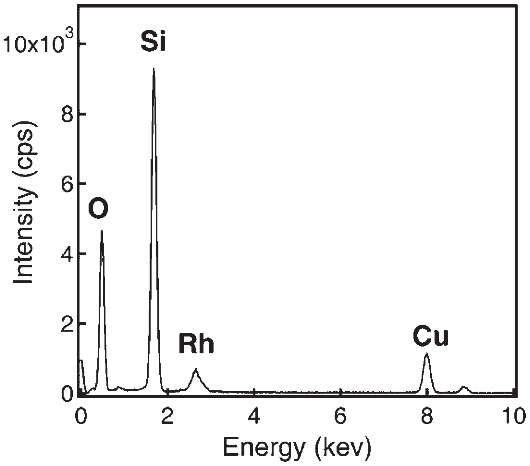


Figure 6. EDAX results of sample SBA-Rh.

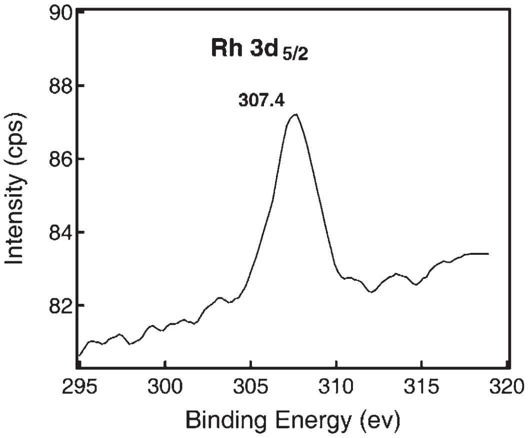
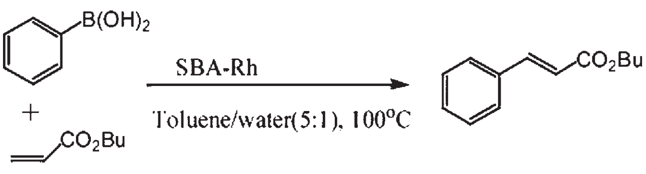


Figure 7. XPS spectrum of sample SBA-Rh.

copy analysis of X-rays (EDAX) (Figure 6), which reveals a Rh content of about 5.1 wt% on average.

Figure 7 shows the X-ray photo-electron spectrum of SBA-Rh in the Rh $^3d_{5/2}$. The Rh $^3d_{5/2}$ peak is centered at 307.4 eV. This binding energy matches well with that of Rh(0) $^3d_{5/2}$ and no obvious peak of Rh^{2+} was observed, which indicates that the rhodium element has been totally reduced and confined on the surface of the matrix.

The SBA-Rh material was applied to catalyze the Heck type carbon-carbon coupling reactions of phenylboronic acid and *n*-butyl acrylate in a toluene/water (5:1) mixture (Scheme 2) under base-free conditions. The reactions were conveniently carried out in a reactor at 100 °C under a nitrogen atmosphere. The yield of product with respect to reaction time and amount of catalyst showed that the SBA-Rh catalyst has an excellent activity for carbon-carbon coupling reactions although there also exist traces of the 1,4 Michael addition product. Investigation of the reaction kinetics of phenylboronic acid with *n*-butyl acrylate (Figure 8) showed an instantaneous reaction and a yield of 85% was obtained after 3 h reaction. The catalytic activity was much stronger than that reported before.[11] This may be due to the high dispersion of the catalyst species: if the outer and the pore surface of the mesoporous matrix is assumed to be fully covered with a rhodium colloidal layer, the specific area of the catalyst calculated in rhodium can be as high as 7000 $m^2 g^{-1}$. Although catalytic species also exist on the outer surface of the matrix, Rh element was not detected in the final mixture by ICP (less than 0.1 ppm of the detecting limit) after reaction.



Scheme 2. Heck- type coupling reactions between phenylboronic acid and *n*-butyl acrylate.

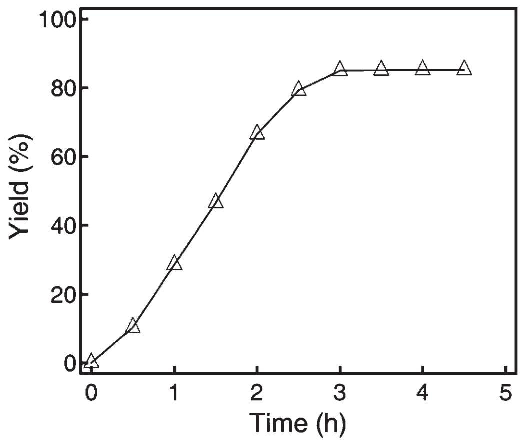


Figure 8. Effect of reaction time on the yield of *n*-butyl phenylacrylate as catalyized by SBA-Rh.

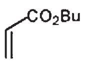
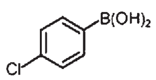
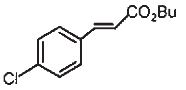
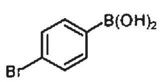
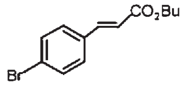
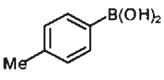
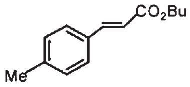
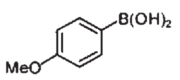
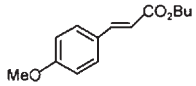
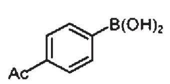
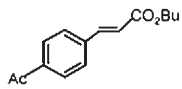
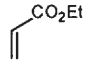
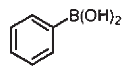
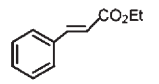
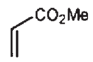
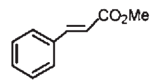
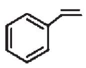
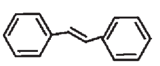
This kind of catalyst also shows very high stability against leaching of the active species into the liquid phase under the given reaction conditions. This feature is very important for a heterogeneous catalyst system. To be sure that the catalytic runs were based on a heterogeneous pathway, in the Heck-type reaction of phenylboronic acid with *n*-butyl acrylate, the catalyst was removed after 2 h of reaction by hot filtration and the reaction was allowed to continue under the identical reaction conditions for an additional 10 h and analyzed for further conversion. The Heck-type reaction totally stopped upon the catalyst removal, indicating that the Heck reaction investigated followed a heterogeneous pathway.

The SBA-Rh catalyst recycling studies were also performed using the same reaction by recycling and then reusing the catalytic materials under the same conditions. Before reuse, the solid was separated from the reaction medium by filtration, washed with dichloromethane and finally dried at 40 °C. The reaction conversion (Table 2) shows that the immobilized catalyst can be repeatedly used without any apparent decrease in its catalytic activity. At the same time, the rhodium content in the fresh and used catalyst after 5 cycles was found to be almost the same (Rh in the fresh catalyst: 0.50 mmol g^{-1} and in the used catalyst after 5 cycles: 0.498 mmol g^{-1} analyzed by ICP). These studies clearly demonstrate that the rhodium is strongly bonded onto the silica surface during the reaction and that the reaction proceeds on the heterogeneous Rh surface.

Table 2. Yield of different cycles.

Cycle	1	2	3	4	5
Yield [%]	85	84	83	82	83

Table 3. SBA-Rh-catalyzed coupling of aryboronic acids with olefin.

Olefin	Arylboronic acid	Product	Time h	Yield %
			5	77
			5	82
			3	85
			3	90
			9	78
			3	89
			3	89
			5	70

All reactions were carried out in N2 atmosphere with 0.125 mol% SBA-Rh as catalyst.

Table 3 lists the results of other catalytic reactions between acrylates and arylboronic acids. The SBA-Rh showed high catalytic activity for this type of reaction. Compared to the analogous Rh-supported silica gel catalyst SiO_2-Rh,[11] SBA-Rh shows relatively high catalytic activity in Heck type reactions. It only needs about one-fifth of the amount of catalyst and less reaction time to reach the same conversion under the same reaction conditions. We attributed this to the high dispersion of rhodium in a form of ultra-thin colloidal layers on the pore surface of the host. Advantages of the SBA-Rh catalyst were that the synthesis is very simple and the rhodium metal could be almost fully recovered after reactions. This method also can be used in preparing other noble metal-grafted mesoporous catalysts.

In conclusion, a new heterogeneous catalyst system, SBA-Rh, has been successfully prepared by an *in-situ* reduction method. Mesoporous SBA-15 was used as the support without any pre-modification. The introduction of hydrosilane functions on the surface resulted in highly dispersed Rh metal colloidal layer both on the inner and outer surfaces of the support material, providing excellent catalytic activity for Heck-type carbon-carbon coupling reactions in organic and water mixed solvent.

Experimental Section

The mesoporous silica SBA-15 was synthesized according to the literature using tri-block poly(ethylene oxide)-poly-(propylene oxide)-poly(ethylene oxide), $EO_{20}PO_{70}EO_{20}$, as a template in acidic conditions.[14] The mesoporous silicon SBA-15 was directly used as support without any pretreatment. After being functionalized with trimethoxysilane on the pore surface (SBA-H), the mesoporous material was treated with 0.05 mol/L $Rh_2(OAc)_4$ THF solution and then filtered, dried in vacuum at room temperature which gave a gray rhodium-containing powder (SBA-Rh).

Preparation of SBA-H

SBA-15 (1.5 g) was dispersed in dry CH_3Cl (50 mL) and $(CH_3O)_3SiH$ (10 mL) was added dropwise under stirring. The mixture was filtered after being fluxed under an N_2 atmosphere for 24 h. The solid obtained after repeated washing with CH_3Cl was named SBA-H.

Preparation of Rh-SBA

SBA-H (1.5 g) was dispersed in dry THF (20 mL); 0.05 M $Rh_2(OAc)_4$ THF solution (30 mL) was added slowly afterwards. After stirring for 4 h, the solid was filtered, washed with THF and dried in vacuum at room temperature.

Catalytic Studies

In a typical experiment, phenylboronic acid (10 mmol), *n*-butyl acrylate (30 mmol), SBA-Rh (100 mg) and toluene-water (5:1) (30 mL) were combined in a 100-mL three-necked flask, followed by addition of 30 mL mesitylene as internal standard for GC analysis. The reaction mixture was stirred at 100 °C under nitrogen for the specified time period. The resulting materials were analyzed by GC-MS.

Characterization

X-ray diffraction (XRD) data were collected on a Rigaku Rint- 2000 diffractometer with a graphite-monochromatized Cu Kα radiation ($\lambda = 0.15405$ nm). High resolution transmission electron microscope (HR-TEM) observations and energy dispersive spectra (EDS) were performed on a field emission JEM-3000F (JEOL) electron microscope operated at 300 kV and equipped with a Gatan-666 electron energy-loss spectrometer and energy-dispersive X-ray spectrometer. N_2 adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP2020 system. The specific surface area and the pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. FT-IR spectra were obtained on Nicolet 7000-C with 4 cm^{-1} resolution. Powder samples were dispersed in KBr pellets for IR analysis. X-ray photoelectron spectra (XPS) were recorded on a Physical Electronics XPS-5700 spectrometer with Al Kα X-ray line (1486.6 eV). Content of Ru in the solution was determined by inductively coupled plasma (ICP) atomic emission spectroscopy (SEIKO SPS1700HVR).

Acknowledgements

This work was supported by National Nature Foundation of China (Grant no. 20633090)

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