Synthesis and CO Oxidation Catalytic Character of High Surface Area Ruthenium Dioxide Replicated by Cubic Mesoporous Silica

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A high surface area ruthenium dioxide with partial ordered structure has been replicated by cubic *Ia*3*d* mesoporous silica, and the replica shows high catalytic activity for the oxidation of CO to CO_2 at relatively low temperature.

The catalytic oxidation of carbon monoxide to carbon dioxide at low temperature and under ambient pressure is a key process for the removal of CO from automotive exhaust and the industrial pollution abatement. Numerous studies were performed to enhance the catalytic oxidation of CO at low temperature, and it was found that the noble metals such as Au, Pd, Pt, and Ru nano-particle supported on various metal oxides show excellent low temperature catalytic activity for this reaction.[1,2] Ruthenium dioxide attracts great attention because of the application in many fields, such as electro-catalytic applications, high-energy storage, and hetero-catalytic system.[3–5] Recent research reported that hydrous ruthenium dioxide is a very active catalyst in the oxidation of CO reaction, however this material suffers from decomposition upon heating.[6] The sol–gel method was adopted for the preparation of high surface area ruthenium dioxide, however the poor thermal stability and poor crystallinity limit its application in some fields.[7] In recent years, more and more attention has been paid to the investigations of hard template synthesis of novel nanostructured materials. Ordered mesoporous silica has been employed as a hard template for the synthesis of other porous materials, because of its special characters of uniform mesopore, high surface area, and large pore volume. The synthesis of various metal, carbon, metal oxide, and semiconductor nanoporous or nanoarray materials has been reported by this approach.[8–12] Hereby, we report for the first time the synthesis of RuO_2 with high surface area and partially ordered framework, using the cubic *Ia*3*d* mesoporous silica KIT-6 as hard template. The RuO_2 replica shows high catalytic activity for the oxidation of CO at relatively low temperature.

The cubic *Ia*3*d* mesoporous silica KIT-6 was prepared according to the method described in the literature.[13] To obtain the surfactant-free hard template with abundant silanol group on the interior surface, the surfactant was removed by solvent extraction using ethanol refluxing method under stirring for 10 h, followed by oxidization using 15 wt % H_2O_2 solution under stirring for 5 h at 37 °C. The surfactant-free product was filtered, washed with ethanol, and dried at 60 °C in vacuum. The ruthenium dioxide replica was prepared using the as-prepared KIT-6 as the hard template and $RuCl_3 \cdot 2H_2O$ as the ruthenium source by two steps impregnation. In a typical synthesis, 0.3 g of $RuCl_3 \cdot 2H_2O$ was dissolved in 5 mL of ethanol. This solution was incorporated into 0.2 g of mesoporous silica by the incipient wetness technique. After the ethanol was evaporated at 60 °C, the composite was exposed to the vapor of ammonia solution (25 wt %) for 10 h in order to covert the precursor to hydrous ruthenium oxide and followed by calcination at 350 °C in order to remove the ammonium chloride. The above process was repeated with different amount of precursor −0.2 g of $RuCl_3 \cdot 2H_2O$. The final composite was obtained by calcination at 350 °C for 5 h. The silica template of the composite was removed by washing with heated 1–2 M NaOH solution for several times. The template-free RuO_2 product was washed by distilled water, collected by centrifugation and dried at 100 °C.

The catalytic reactions were conducted in a temperature-programmed reaction system using a thermal conductivity detector (TCD) of a gas chromatograph (HP 6890 series GC system). In a typical reaction, 100 mg RuO_2 replica was loaded in a quartz tube reactor, and the reactor could be heated from room temperature to 350 °C at a rate of 6 °C/min. The total gas flow amounted to 50 mL/min, and the volume ratio of the gas is $CO:O_2:He = 1:5:44$.

The small-angle X-ray diffractions (XRD) pattern of the mesoporous silica KIT-6 (not shown) exhibit well-resolved peaks, which are all accounted with the cubic *Ia*3*d* symmetry

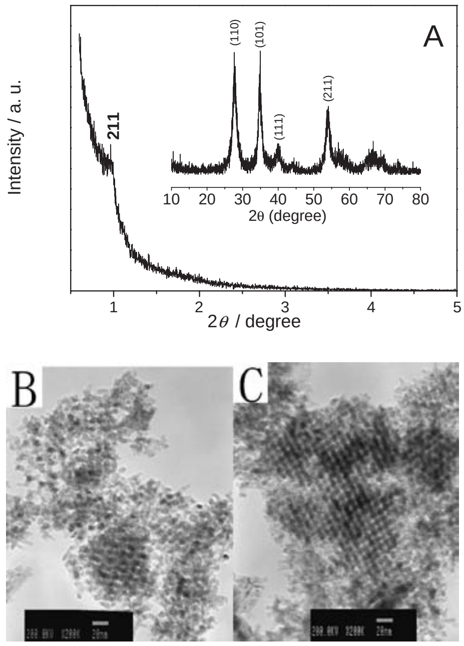

Figure 1. (A) Small-angle XRD pattern of the ruthenium oxide replica, and the inset is the wide-angle XRD pattern, (B) and (C) The TEM images of the ruthenium oxide replica obtained on JEM2010 electron microscope operated at 200 kV, the ordered part of the (B) image is the view of the [311] direction and the (C) image is view of the [110] direction.

with lattice spacing $a = 24.74$ nm. The N_2 sorption isotherms of the synthesized mesoporous silica display a typical character of mesopores, and the BET specific surface area, pore volume, and pore size is 852 m^2/g, 1.37 cm^3/g, and 6.85 nm, respectively.

The energy-dispersive spectroscopy (EDS) measurement (not shown) performed on different domains of the template-free RuO_2 replica, reveals almost complete removal of silica template, as only trace amount of silicon can be detected. Figure 1a illustrates the small-angle and the wide-angle (inset) XRD pattern of the RuO_2 replica. Only one weak characteristic peak can be found, which could be assigned to the diffractions of the (211) of the *Ia*3*d* symmetry, suggesting that the replica posses some grade of ordering. The wide-angle XRD pattern shows slightly broadened Bragg diffraction peaks, which can be indexed to a rutile phase ruthenium oxide, indicating that the well-crystallized framework of the replica. The N_2 sorption measurement reveals that the BET specific surface area of the replica ruthenium oxide is as high as 73.4 m^2/g, and the pore volume is 0.254 cm^3/g, which are all consistent with other metal oxide replica reported in literature.[10] However, in the N_2 sorption isotherm, the characteristic jump indexed to the capillary condensation of mesopores is unclear, and the average pore diameter calculated by BJH method is 13.9 nm. The transmission electron microscope (TEM) images of the replica ruthenium oxide, as shown in the Figures 1b and 1c, also indicate that the ruthenium oxide replica display a partially ordered framework. The ruthenium oxide replica is composed of ordered framework segments and disordered nanorods, and the diameter of the rods is about 6–7 nm, which is accord with the pore size of the hard template (6.85 nm), which indicate that the framework or the nanorod is a replica of the pore of the silica template. It can be seen from the TEM images that the ordered segments are approximately close to the cubic *Ia*3*d* symmetry, but the range of ordering is small. This can explains the low small-angle XRD peak intensity and the unclear N_2 sorption jump but high surface area of the RuO_2 replica.

This ruthenium oxide replica shows high catalytic activity for the oxidation reaction of CO to CO_2 at low temperature. The as-synthesized ruthenium oxide replica was directly used as catalyst without any treatment. The conversion of the CO over the RuO_2 replica is shown in the Figure 2, the temperature at the turning point being regarded as the temperature at which the CO oxidation is completed. The RuO_2 replica in the first catalytic reaction cycle shows relatively low catalytic activity, and the complete CO oxidation is achieved at about 165 °C. This is probably due to the presence of oxygen vacancies on the surface of the as-synthesized RuO_2 replica since a larger amount of oxygen was consumed by the sample during the first CO oxidation cycle than during the subsequent cycles at the completed CO oxidation temperature in the first cycle. It can be seen that the quickly accelerated CO conversion occurs in the following cycle below 75 °C, and complete CO oxidation is achieved at 90 °C in the second cycle, and in the third and fourth cycles, the complete CO oxidation is stably achieved at 105 °C, indicating the sustained catalytic activity. As the each cycle ends at 350 °C, the prepared RuO_2 catalyst is at least catalytically stable at as high as 350 °C. This unusual catalytic behavior differs from the previous finding[6] in which hydrous ruthenium oxide is used as catalyst and the catalyst dried at 150 °C shows the highest catalytic activity in the room temperature. A detailed study on the mechanism of the catalytic process is under way.

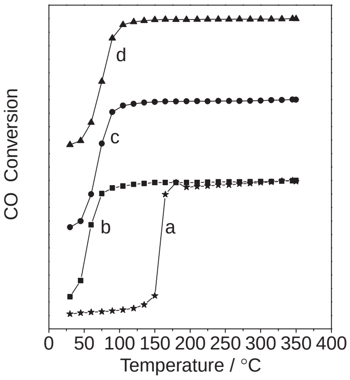

Figure 2. The conversion of CO over the ruthenium oxide replica for the first a), second b), third c), and fourth d) catalytic reaction cycle.

In summary, we have synthesized high surface area ruthenium oxide using the cubic *Ia*3*d* mesoporous silica KIT-6 as the template. The ruthenium oxide replica is a mixture of ordered framework segment and disorder nanorods. It shows high catalytic activity for the oxidation reaction of CO to CO_2 at low temperature, and the complete CO oxidation temperature on this replica is stable at about 105 °C. With respect to the special character of RuO_2 and the large surface of this replica, it is potentially applicable in other domains such as electrocatalysis and supercapacitors.

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