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Potassium promoted Ru/meso-macroporous SiO₂ catalyst for the preferential oxidation of CO in H₂-rich gases

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ABSTRACT

A series of potassium promoted Ru/meso-macroporous SiO₂ catalysts were prepared and used for the preferential oxidation of CO (CO-PROX) in H₂-rich gases. The catalysts were characterized by using techniques of TEM, SEM TPR, XPS, and N₂ adsorption/desorption. The catalytic activity of Ru/meso-macroporous SiO₂ was markedly improved by the introduction of potassium. The catalyst of K-5 wt.% Ru/meso-macroporous SiO₂ with molar ratio of K:Ru = 5:7 exhibited relatively high activity and selectivity for CO-PROX. Nanoparticles of ruthenium species can be highly dispersed on the meso-macroporous SiO₂ support by the simple impregnation method. The addition of potassium weakened the interaction between metallic Ru and the silica support. Lowering the reduction temperature of ruthenium ions could keep ruthenium in the state of metallic Ru, and it was proposed that potassium acted as an electron donating agent. The electron donating effect of potassium improved the low temperature activity for CO oxidation and increased the selectivity of O₂ for CO oxidation, thus K-modified Ru/meso-macroporous SiO₂ catalyst showed obviously a wide temperature window for CO elimination from H₂-rich gases, meanwhile the related mechanism was discussed.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) seems to be one of the most affordable and commercially viable hydrogen-based fuel cells, which possesses many attractive features, such as high power density, rapid start-up, and high efficiency [1]. PEMFC is fueled with hydrogen that is generally produced by steam reforming of hydrocarbons and followed with water–gas shift reaction [2]. Thus generated H₂-rich gases generally contain about 1 vol.% CO. However, the anode of PEMFC is sensitive for the poisoning effect of trace amount of CO. The residual concentration of residual CO must be decreased to less than 100 ppm for the CO-resistant anodes

[3]. As for the application of the small-scale fuel processor, the selective diffusion separation by membrane, the selective CO methanation, and the preferential oxidation (PROX) of CO had been considered to be promising methods for purifying CO from the H₂-rich gases, among them PROX was regarded as the most promising way [4].

Up to present, much work has concentrated on developing highly active and selective catalysts for CO-PROX. The catalysts reported include noble metal catalysts, such as Pt [5], Ru [6] and Au [7] and base metal oxide catalysts, such as CuO/CeO₂ [8] and Co₃O₄ [9]. Conventional supports including CeO₂ [10], Al₂O₃ [11], SiO₂ [12], zeolite [13], and activated carbon [14] were studied for the preferential oxidation of CO in H₂-rich gases.

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The activity of supported Ru catalyst for CO-PROX had been investigated, and the catalysts showed good activity at low reaction temperature. Michael D. Amiridis and co-workers [6] studied the effect of Ru precursors, the preparation methods and the pretreatment conditions on the catalytic performance of Ru/SiO₂. They pointed out that the combination of a direct hydrogen treatment and using a nitrate precursor resulted in the synthesis of finely dispersed Ru catalysts. The residual CO could be eliminated completely in the temperature range of 120–150 °C over the Ru/SiO₂ catalyst with a gas mixture of 0.5% CO, 0.5% O₂, 45% H₂, balanced with N₂. When the catalyst of bimetallic Pt–Ru/SiO₂ was directly reduced in H₂ at 300 °C, its catalytic behavior was similar to that of Ru/SiO₂. The Pt–Ru/SiO₂ catalyst could reduce the residual concentration of CO to less than 1 ppm in the temperature range of 120–150 °C in H₂-rich gases without H₂O and CO₂. The addition of Pt stabilized Ru nanoparticles and prevented its sintering in oxidizing conditions [15]. The CO-PROX in H₂-rich gas over K₂CO₃-promoted Rh/SiO₂ (K₂CO₃-Rh/SiO₂) catalysts was investigated [16], and the results were compared with those of Rh/SiO₂ catalysts. K₂CO₃-Rh/SiO₂ catalysts were able to realize almost complete removal of CO in the temperature range of 140–160 °C. The additive effect of K₂CO₃ depended on the preparation method and the amount of K₂CO₃. K₂CO₃-Rh/SiO₂ catalyst prepared by the sequential impregnation method with a 3:1 molar ratio of K/Rh exhibited the best performance. According to the characterization results, metal particles in the catalyst Rh were highly dispersed and partially covered by K₂CO₃. The catalytic behavior of Ru is similar to that of Rh in many reactions, so potassium may also make a good promoter of Ru/SiO₂ for CO-PROX. However, to the best of our knowledge, reports on the alkali metal promoted-Ru/SiO₂ for the CO-PROX have not been found.

In the early 1990s, the ordered mesoporous materials with pore sizes above 2 nm were reported [17]. Years later, macroporous materials had also attracted much attention in the later 1990s. Recently, studies on meso-macroporous materials and their applications to catalysis are pretty active. Kaliaguine [18] reported the macroporous materials with mesoporous MCM-48 walls, which exhibited high surface area. As for solid catalysts, introducing meso-macroporosity can effectively increase the specific surface area, the macropores favor mass and heat transfer.

In this work, meso-macroporous SiO₂ monoliths were prepared, characterized and used as the catalyst support for CO-PROX reaction. A tri-block copolymer (P123) poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) and polystyrene (PS) foam were used as the template for the mesopores and the macropores, respectively. Meanwhile, the effect of potassium doping for Ru/SiO₂ was investigated. The prepared potassium–Ru/meso-macroporous SiO₂ exhibited excellent catalytic activity for CO-PROX.

2. Experimental method

2.1. Preparation of meso-macroporous SiO₂

The PS foams were obtained from polymerization of styrene in highly concentrated water-in-oil (W/O) emulsions. When the

highly concentrated W/O emulsion was generated, the emulsion was put in a glass mold and polymerization of styrene occurred. Then the wet polystyrene monoliths were dried at 60 °C for 24 h to obtain polystyrene monolithic templates, and details were stated in Ref. [19].

The meso-macroporous SiO₂ monoliths were prepared by sequential impregnation of PS foam with silicon oxide hydrosol. At first, P123 was added into distilled water and dispersed by ultrasonic agitation at room temperature for 2 h. Then HCl (2 mol l⁻¹) was dropped into the above suspension and whereafter was sonicated for 1 h. After that, tetraethyl orthosilicate (TEOS) was added into the above mentioned solution at 30 °C for 5 h to form silicon hydrosol. Then, the PS template was impregnated into the hydrosol under vacuum condition until no air bubble escaped from the PS template. The impregnated sample was dried at 60 °C for 24 h. This impregnation step was repeated for several times. The obtained dried sample was calcined in N₂ at 600 °C for 4 h to remove P123 and PS template. And the meso-macroporous SiO₂ monolith was obtained.

2.2. Preparation of potassium promoted Ru/meso-macroporous SiO₂ catalysts

The meso-macroporous SiO₂ monoliths were crushed into a 40–60 mesh, which kept the meso-macroporous structure after the crush. The potassium–Ru/meso-macroporous SiO₂ was prepared by the co-impregnation of the meso-macroporous SiO₂ support with a mixed aqueous solution of ruthenium nitrosyl nitrate (Ru(NO)(NO₃)₃·xH₂O) and K₂CO₃. Following the impregnation, samples were freeze-dried overnight. Ru/meso-macroporous SiO₂ was prepared with the impregnation method using Ru(NO)(NO₃)₃·xH₂O solution. The weight fraction of Ru was defined as Ru wt.% = [M]_{Ru} / ([M]_{Ru} + [M]_{SiO₂}), in which [M]_{Ru} is the weight of metal Ru in the catalyst and [M]_{SiO₂} is the weight of SiO₂ support.

2.3. Catalyst characterizations

Nitrogen adsorption and desorption isotherms were measured on a Micromeritics apparatus of model ASAP-2020 at –196 °C. The specific surface areas were calculated according to the BET method and the pore size distributions were determined from the adsorption branch of the isotherm with BJH model.

Temperature programmed reduction (TPR) experiments were carried out on a quartz reactor with a reduction gas mixture of 5 vol.% H₂/Ar at a heating rate of 10 °C min⁻¹. 50 mg of sample was loaded in a quartz reactor. Before analysis, the sample was reduced in a gas mixture of 5 vol.% H₂/Ar at 300 °C for 2 h and oxidized in air at 150 °C for 1 h.

Scanning electron microscopy (SEM) characterizations were performed on a Hitachi S4800 field-emission scanning electron microscope with Au-sputtered specimen operated at 15 keV to observe the macroporous structure of the samples.

Transmission electron microscopy (TEM) was performed on a Technai G² F20 microscope operated at 200 kV. Samples were pre-reduced at 300 °C in a gas mixture of 5 vol.% H₂/N₂ for 2 h, then finely grounded in a mortar to fine particles and dispersed ultrasonically in ethanol. The well-dispersed

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