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Catalytic performance of Ru nanoparticles supported on different mesoporous silicas for preferential oxidation of CO in H_2-rich atmosphere

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ABSTRACT

Ru catalysts supported on different mesoporous silicas, MCM-41, MCM-48, SBA-15 and KIT-6, were applied to the preferential oxidation of CO in a H_2-rich atmosphere (PROX). The properties of mesoporous support and the supported Ru catalysts were investigated using N_2 physisorption, FTIR, TEM, CO chemisorption, H_2-TPR and XPS. The performance of Ru catalysts in PROX highly relates to the Ru dispersion, support pore structure, Ru reducibility and the interaction between Ru and support. Ru/KIT-6 presents the highest surface activity (TOF values), owing to the easiest reducibility of Ru. Nevertheless, its poor Ru dispersion results in a low number of surface active sites, leading to the low CO conversion value over Ru/KIT-6. Ru/MCM-41 can achieve full CO conversion and the high CO_2 selectivity in the reaction temperature range of 115–180 °C owing to the high Ru dispersion from the strong interaction between Ru and MCM-41.

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1. Introduction

Fuel cells have been drawing intensive interests worldwide because of converting chemical energy directly into electricity efficiently and environmental friendly. Among different types of fuel cells, the polymer electrolyte membrane fuel cells (PEMFCs) show some advantages, such as low operation temperature, high power density and easy start-up [1]. PEMFCs utilize high purity hydrogen as the energy source, which is conventionally produced from steam reforming, partial oxidation or auto-reforming of alcohols and hydrocarbons [2]. However, a significant amount of CO is also formed as a by-product, and even after a subsequent water-gas-shift process, the CO concentration is still around 0.5–1.0 vol.% [3]. CO impurity, even at a concentration as low as 10 ppm, can poison the noble metal electrodes and deteriorate the electrical performance [1,4]. Therefore, CO methanation or preferential oxidation of CO (PROX) has to be employed to achieve the further reduction of CO concentration to an acceptable ppm level. Considering the higher amount of H_2 consumed in methanation, PROX is a more suitable way for CO removal.

A wide range of catalysts for the PROX have been reported, including non-noble metal oxides (CuO [5], NiO [6], Co_3O_4 [7]), noble metals [8] (Pt [9,10], Pd [11], Au [12–14], Rh [15–18], Ru [19–21]) and multiple metallic systems [22,23]. Not only powder catalysts, some pellet catalysts in lab-scale channel reactors have already developed and applied for PROX reaction [24,25]. Among these reported catalysts, Ru-based catalysts possess high activity and selectivity at a lower temperature range (below 150 °C) [26,27]. Two support materials, SiO_2 and Al_2O_3, have been compared for PROX catalytic performance after loading with Ru catalysts. It was found that the temperature of the CO light-off curve of Ru/SiO_2 was about 30 °C lower than that of Ru/Al_2O_3, which was attributed to the lower stability of the adsorbed CO species on the former than the latter and facilitating the CO reaction on the surface [28].

Mesoporous silicas have been extensively investigated in the catalysis field because of their well-ordered porosity, high thermal stability and large surface area [29], however, only a few applications in PROX reaction have been reported. Fukuoka et al. [30,31] used Pt nanoparticles supported on FSM-16 and FSM-type mesoporous silica in the PROX reaction and found that the PROX activities were closely related to the pore diameter and the surface silanol groups of the support. The surface silanols are suggested to play as “oxidant” to initiate CO oxidation [2]. Other mesoporous silicas, such as HMS, SBA-15, SBA-16 and MCM-41, were also used to support active phases, e.g. Au, Pt and CuO, in the PROX reaction [32–35]. However, Ru nanoparticles supported mesoporous silicas, on the basis of our knowledge, have not been reported in PROX up to now and no comparison work has been conducted over different mesoporous siliceous supports with different pore structures.

In this work, Ru nanocatalysts supported on templated mesoporous siliceous materials with different pore structures were prepared and their catalytic activities in PROX reaction were

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compared. The siliceous supports in this work are silicas possessing with unidirectional cylindrical mesopores of various diameters, MCM-41 and SBA-15, and silicas with three-dimensional cylindrical channels of different sizes, MCM-48 and KIT-6.

2. Experimental

2.1. Catalyst preparation

The mesoporous siliceous materials were synthesized by hydrothermal treatment. For MCM-41 and MCM-48, cetyltrimethylammonium bromide (CTAB, 99%, Sigma–Aldrich) was employed as templates, and tetraethyl orthosilicate (TEOS, 98%, Sigma–Aldrich) was used as silicon source. Their synthesis followed a published procedure [36]. For SBA-15 and KIT-6, A tri-block copolymer (P123, Sigma–Aldrich) poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) was utilized as structure directing agent according to the procedure described before [37,38].

Ru catalysts supported on the mesoporous silicas, were prepared by wet impregnation method. Firstly, mesoporous silicas (0.5 g) were dispersed in a $RuCl_3$ acetone solution of 75 ml (to achieve Ru loading of 2 wt.%) by sonication for 100 min. After ultrasonic treatment the mixture was stirred at room temperature (RT) until the acetone was evaporated. The $RuCl_3$/silica samples were heated at 1 °C/min to 110 °C in air, held at 110 °C for 11 h, and then reduced at 450 °C for 5 h in a flow of H_2/Ar. The synthesized catalysts were denoted as Ru/MCM-41, Ru/MCM-48, Ru/SBA-15 and Ru/KIT-6 accordingly.

2.2. Characterization

N_2 physisorption isotherms of the samples were obtained using a Micromeritics TriStar 3020 at −196 °C, after degassing samples for 24 h at 175 °C. The corresponding specific surface areas (S_g) were calculated by the Brunauer–Emmett–Teller (BET) equation at relative pressure ($P/P^ø$) between 0.05 and 0.35. Total pore volumes (V_p) were evaluated at relative pressures ($P/P^ø$) close to unity. Pore size distributions (PSD) were calculated from desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method.

Fourier transformer infrared spectroscopy (FTIR) was conducted with a PerkinElmer Spectrum 100 FTIR spectrometer under attenuated total reflectance (ATR) mode. The mesoporous siliceous supports were examined under transmission electron microscopy (TEM) on a JEOL JEM-1010 microscope with accelerating voltages of 100 kV, while to obtain a higher resolution, the supported Ru catalysts are observed under JEOL JEM-2100 microscope at accelerating voltages of 200 kV. The samples were dispersed by ultrasonication in a mixture of ethanol and isopropanol, and then deposited on a holey carbon grid and dried. A Kratos Axis ULTRA X-ray Photoelectron Spectrometer (XPS) was used to measure the binding energy of the Ru atoms incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was Monochromatic Al Kα X-rays (1486.6 eV) at 225 W (15 kV, 15 mA). The C1s peak position was set to 284.8 eV and taken as an internal standard.

CO-chemisorption was conducted using the pulse injection measurement in a U-shaped quartz reactor on Belcat instrument with thermal conductivity detector (TCD). 50 mg of each sample was reduced in H_2 at 200 °C for 30 min and then purged with He for 10 min. After the purge, the sample was cooled to 50 °C, and then in He at 50 °C, 5% CO/He was injected automatically using an electromagnetic six-way valve with a loop of 1.0 ml. The pulse injection was repeated until saturation of CO was observed. The adsorbed moles of CO was measured and used to calculate the dispersion of Ru particles. The stoichiometry factor of CO/Ru is assumed to be 1 in our study.

Temperature programmed reduction with hydrogen (H_2-TPR) experiments of the samples were also performed on Belcat. Prior to each measurement, the sample of 50 mg supported Ru catalyst was heated from RT to 500 °C in a heating rate of 10 °C/min under an Ar flow of 50 ml/min (STP), and then oxidized in 5% O_2/He flow at 500 °C for 60 min. After that, the temperature was decreased to RT in Ar flow, and the gas flow was switched to 5% H_2/Ar of 30 ml/min (STP). Finally, TPR profiles were obtained with a temperature ramp of 10 °C/min. Before entering TCD, the gas flow from the TPR reactor was passed through a trap filled with 5A zeolite to eliminate water produced during reduction process.

2.3. Activity test

PROX reactions were performed in a vertical stainless steel tube reactor (7.5 mm inner diameter). Firstly the catalyst sample was heated in an Ar flow from RT to 400 °C in a heating rate of 5 °C/min and then the gas was switched to H_2 for reduction for 60 min at 400 °C. After that, the temperature of the sample was adjusted in an Ar flow to the pre-set value for PROX and the gas flow was switched to reaction gas with a composition of 1 vol.% CO, 1 vol.% O_2, 15 vol.% CO_2 and 20 vol.% He, balanced in H_2. Each reaction temperature is maintained for at least 1 h to obtain the steady state. All the experiments were performed at atmospheric pressure and the temperature was measured using a thermocouple inserted into the catalyst bed. The product gas was analyzed with a Shimadzu GC-8A gas chromatograph equipped with a TCD and a carrier gas of H_2. Two columns, Molsieve 5A column and Carbosphere column, are used to quantify O_2 and CO and CO_2.

Since the change in total gas volumetric flow rate after the reaction was relatively small and can be regarded as negligible here, CO conversion, O_2 conversion, and CO_2 selectivity for PROX reaction were calculated as below:

$$\text{CO conversion}\,(\%) = \frac{M[\mathrm{CO}]_{\mathrm{in}} - M[\mathrm{CO}]_{\mathrm{out}}}{M[\mathrm{CO}]_{\mathrm{in}}} \approx \frac{[\mathrm{CO}]_{\mathrm{in}} - [\mathrm{CO}]_{\mathrm{out}}}{[\mathrm{CO}]_{\mathrm{in}}} \times 100$$

$$\mathrm{O_2}\ \ \text{conversion}\,(\%) = \frac{M[\mathrm{O_2}]_{\mathrm{in}} - M[\mathrm{O_2}]_{\mathrm{out}}}{M[\mathrm{O_2}]_{\mathrm{in}}} \approx \frac{[\mathrm{O_2}]_{\mathrm{in}} - [\mathrm{O_2}]_{\mathrm{out}}}{[\mathrm{O_2}]_{\mathrm{in}}} \times 100$$

$$\mathrm{CO_2}\ \ \text{selectivity}\,(\%) = \frac{0.5 \times ([\mathrm{CO}]_{\mathrm{in}} - [\mathrm{CO}]_{\mathrm{out}}}{[\mathrm{O_2}]_{\mathrm{in}} - [\mathrm{O_2}]_{\mathrm{out}}} \times 100$$

where $M[X]_{in}$ and $M[X]_{out}$ are the molar flow rates of X component at the reactor inlet and outlet, respectively, while $[X]_{in}$ and $[X]_{out}$ represent the corresponding X concentration in the gas mixture. CO_2 selectivity is defined as the ratio of O_2 consumption for CO oxidation over the total O_2 consumption and was only reported when CH_4 was not formed.

In order to ensure the reaction is performed in the kinetically controlled regime, the external and internal diffusion influences have been investigated (see Supplementary material), and then the reaction conditions (catalyst amount: 0.2 g; reaction gas flow rate: 63 ml/min, catalyst particle size: 90–125 μm) were chosen for the activity test.

3. Results and discussion

3.1. Catalyst characterizations

3.1.1. Nitrogen physisorption

Fig. 1 depicts the nitrogen adsorption–desorption isotherms and pore size distributions of both mesoporous silicas and the corresponding supported catalysts. All the four siliceous supports exhibit a type IV isotherm based on IUPAC classification [39], which is the typical isotherm of mesoporous materials. MCM-41 and

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