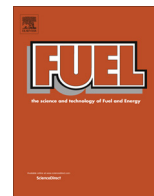




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Ru/TiO₂ for the preferential oxidation of CO in H₂-rich stream: Effects of catalyst pre-treatments and reconstruction of Ru sites

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HIGHLIGHTS

- Ru/TiO₂ exhibits remarkable catalytic performance in the reaction of CO PROX for fuel cell application.
- The catalyst preparation and pre-treatment show great impacts on the catalytic performance.
- Isolated metallic Ru species are identified as preferred active sites in CO PROX.
- Linear monocarbonyls are determined to be key reaction intermediates in CO PROX.

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ABSTRACT

The preferential oxidation (PROX) of CO is a promising strategy for trace CO clean up in H₂-rich stream to fuel cells. In the present study, a series of TiO₂ supported clusters were prepared and studied for the PROX of CO. Amongst, Ru/TiO₂ catalyst exhibited remarkably high PROX activity in the operation temperature range of fuel cells. The effects of catalyst preparation and pre-treatment on the catalytic performance of Ru/TiO₂ were investigated in detail. Ru/TiO₂ catalyst prepared by photo-deposition and pre-treated under H₂-CO atmosphere was found to be the most promising one and complete CO oxidation could be achieved at >373 K. Ru/TiO₂ pre-treated under different reducing atmospheres were characterized by high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) of CO adsorption. The surface reconstruction of Ru sites during catalyst pre-treatment was observed and isolated metallic Ru species was identified as preferred active sites for PROX reaction. Based on the catalytic and characterization results, the possible mechanism for PROX of CO over Ru/TiO₂ was proposed.

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1. Introduction

In the past decades, extensive attention has been focused on hydrogen as a clean energy resource and ideal energy carrier, which can be applied in fuel cells, e.g. polymer electrolyte membrane fuel cell (PEMFC), to produce electricity efficiently and free of associative pollutants [1–3]. The current large-scale hydrogen source is co-produced with significant amounts of carbon monoxide via the steam reforming and partial oxidation of methane, and carbon monoxide is known as a conventional contaminant to be removed. Although a subsequent water-gas-shift (WGS) reaction can reduce the amount of carbon monoxide to 1%, even low levels of carbon monoxide contained in fuel hydrogen will do great harm to the anodes of fuel cell, e.g. Pt and Pt-based alloys in PEMFC, at

low temperatures, i.e. 353–393 K [4–7]. Thus, it is essential to eliminate trace amounts of carbon monoxide from the reformat stream prior to its introduction into the fuel cell. Several different approaches, such as the selective diffusion, the selective carbon monoxide methanation and preferential oxidation (PROX) of carbon monoxide, have been proposed for the elimination of trace carbon monoxide in hydrogen stream. Among the above-mentioned approaches, PROX appears to be feasible for trace carbon monoxide clean up or bringing down the carbon monoxide concentration from 1% to acceptable level, i.e. below 20 ppm [8,9]. To date, various catalysts, e.g. platinum group metal catalysts [10–14], supported Au catalysts [15,16] and transition metal oxides-based catalysts [17–19], have been explored aiming to improve the carbon monoxide elimination with simultaneous minimizing the loss of hydrogen.

Supported Ru catalysts have been acknowledged as promising candidates for application in PROX due to their outstanding

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activity and selectivity [20–22], however, superior Ru catalysts with enhanced PROX performance are still being explored. Moreover, the PROX performance of Ru catalysts is well debated probably due to the impacts from catalyst constitutions, preparation procedures and catalyst pre-treatment conditions, which consequently leads to an unsatisfying reproducibility for commercial application.

In the present study, a highly-active Ru/TiO₂ catalyst will be optimized for the PROX of carbon monoxide and researches will be focus on the unexpected effects of catalyst pretreatment conditions on their catalytic performance. The structure and electronic state of Ru/TiO₂ catalysts are well characterized by means of high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform Infrared spectroscopy (FTIR) with carbon monoxide adsorption. Based on the results, the surface reconstruction of Ru sites during catalyst pre-treatment can be concluded and the structure–activity relationship of Ru/TiO₂ in PROX will be proposed, which is of great significance for future catalyst design.

2. Experimental

2.1. Preparation of Me/TiO₂ catalysts

Commercial TiO₂ (Degussa P25, 70% anatase, 30% rutile) was used as support and Me/TiO₂ (Me = Cu, Co, Mn, Ru, Au, Ir, Ag, Pt and Pd) catalysts with different metal loadings were prepared by so-called photo-deposition method [23]. The efficiency of photo-deposition is approaching 100% and the actual loadings of metals on TiO₂ are almost identical to the desired loadings, i.e. within measuring errors of ±2%. In a typical preparation of 1% Ru/TiO₂, 2 mM RuCl₃ solution containing 5 mg Ru, 500 mg TiO₂ and 8 mL of methanol were added into a round-bottom quartz flask under stirring to form slurry. The slurry was adjusted to pH 10 ± 0.5 using either 1 M HCl or 1 M NaOH aqueous solution and irradiated by a high-pressure mercury light with the main wavelength of 365 nm for 6 h under the protection of pure nitrogen. Finally, the particles were filtered, dried at ambient conditions and denoted as Ru/TiO₂-p.

For reference, 1% Ru/TiO₂ samples were also prepared by wet impregnation and chemical reduction methods. For wet impregnation, 2 mM RuCl₃ solution containing 5 mg Ru was added to 500 mg of TiO₂ and then the mixture was evaporated in a rotary evaporator at constant temperature of 353 K. The as-obtained particles were carefully washed with deionized water, dried at ambient conditions, and denoted as Ru/TiO₂-i. For chemical reduction, 500 mg of TiO₂ and 2 mM RuCl₃ solution containing 5 mg Ru were added into a round-bottom quartz flask under stirring to form slurry. Then 10 mL of 1 M KBH₄ solution was dropwise added to the slurry under the protection of nitrogen. The particles were filtered, washed with deionized water, dried at ambient conditions and denoted as Ru/TiO₂-c.

The as-prepared Ru/TiO₂ samples were calcined in flowing air at 523 K for 1 h and then subjected to different pre-treatments prior to being used as catalysts in PROX. The pre-treatments were performed at 523 K for 1 h under reducing atmospheres, i.e. 60% H₂ in He (H₂), 1% CO in He (CO) and 1% CO–60% H₂ in He (H₂–CO).

2.2. Catalyst characterization

HRTEM images of samples were acquired by a Philips Tecnai G20 S-TWIN electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the samples were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

XPS were recorded on a Kratos Axis Ultra DLD spectrometer with a monochromated Al Kα X-ray source (*hν* = 1486.6 eV), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). All spectra were recorded by using an aperture slot of 300 × 700 microns. Survey spectra were recorded with a pass energy of 160 eV and high-resolution spectra with a pass energy of 40 eV. Accurate binding energies (±0.1 eV) were determined with respect to the position of the adventitious C 1s peak at 284.8 eV.

FTIR spectra of CO adsorption on Ru/TiO₂ samples were collected on the Bruker Tensor 27 spectrometer with 128 scans at a resolution of 4 cm⁻¹. A self-supporting pellet made of sample was placed in the IR flow cell and the reference spectrum, i.e. background spectrum, was taken at different temperatures. After the He stream was switched to a gas mixture containing 1% CO in He at a total flow rate of 30 mL min⁻¹, a series of time-dependent FTIR spectra of CO adsorption on the samples were sequentially recorded at designated temperatures.

The dispersion of ruthenium on TiO₂ support was determined by CO pulse adsorption on a chemisorption analyzer (Chemisorb 2720, Micromeritics). In a typical experiment, ca. 100 mg sample in the quartz reactor was first reduced in different atmospheres and purged in He at 523 K for 1 h to remove physisorbed molecules on the surface. After cooling down to room temperature in flowing He, pulses of 5%CO/He were injected to the reactor one pulse per minute until no further changes in signal intensity of outlet CO. The dispersion of ruthenium was calculated assuming the equimolar adsorption of CO on ruthenium metal [24].

In situ FTIR spectroscopy studies were performed on the Bruker Tensor 27 spectrometer by using a diffuse reflectance attachment equipped with a reaction chamber (Harrick, Praying Mantis CHC-CHA-3). 128 single beam spectra had been co-added at a resolution of 4 cm⁻¹ and the spectra were presented as Kubelka–Munk function referred to adequate background spectra. The samples were used as self-supporting wafers (ca. 20 mg) and pretreated under different atmospheres at 523 K for 1 h prior to adsorption experiments. After cooling to desired temperature in flowing He, the stream was switched to reactant gas mixture and steady-state FTIR spectra were recorded after time-on-stream of 30 min.

2.3. Catalytic evaluation

The PROX reaction was performed in a fixed-bed flow microreactor at atmospheric pressure. Typically, 0.2 g catalyst (sieve fraction, 0.25–0.5 mm) was placed in a quartz reactor (4 mm i.d.) and pretreated under different conditions. After cooling down to 323 K in flowing He, the reactant gas mixture (1% CO, 1% O₂, 60% H₂ in He) was fed to the reactor. The total flow rate of the gas mixture was kept at 75 mL min⁻¹, corresponding to a GHSV of 22, 500 h⁻¹. The inlet and outlet gases were analyzed on-line by using a Varian CP 3800 gas chromatograph (TCD detector and with molecular sieve 5A and Porapak Q columns for H₂, O₂, CO and CO₂ analysis). Under our reaction conditions, i.e. at relatively low reaction temperatures and in the presence oxygen, the methanation of CO does not occur. Accordingly, the CO conversion and the CO₂ selectivity are calculated based on following equations.

$$\text{CO conversion : } X_{\text{CO}} = \frac{[\text{CO}]_{\text{inlet}} - [\text{CO}]_{\text{outlet}}}{[\text{CO}]_{\text{inlet}}} \times 100\%; \quad (1)$$

$$\text{O}_2 \text{ conversion : } X_{\text{O}_2} = \frac{[\text{O}_2]_{\text{inlet}} - [\text{O}_2]_{\text{outlet}}}{[\text{O}_2]_{\text{inlet}}} \times 100\%; \quad (2)$$

$$\text{CO}_2 \text{ selectivity : } S_{\text{CO}_2} = \frac{X_{\text{CO}}}{2 \times X_{\text{O}_2}} \times 100\%. \quad (3)$$

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