



Selective CO removal in a H₂-rich stream over supported Ru catalysts for the polymer electrolyte membrane fuel cell (PEMFC)

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ABSTRACT

We prepared various Ru catalysts supported on different supports such as yttria-stabilized zirconia (YSZ), ZrO₂, TiO₂, SiO₂ and γ-Al₂O₃ with a wet impregnation method. We applied them to the selective CO removal in a hydrogen-rich stream via the preferential CO oxidation (PROX) and the selective CO methanation simultaneously. Among them, Ru/YSZ showed the highest CO conversion especially at low temperatures. Several measurements: the N₂ physisorption, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), the CO chemisorptions, the temperature-programmed oxidation (TPO), the temperature-programmed reduction (TPR), the temperature-programmed desorption (TPD) of CO₂ with mass spectroscopy and the transmission electron microscopy (TEM), were conducted to characterize the catalysts. No linear correlation can be found between the amount of CO chemisorbed at 300 K and the PROX activity. On the other hand, the facile activation of O₂ appeared to be closely related to the high PROX activity, judging by the TPO experiment. In addition, the strong adsorption of CO₂ suppressed the low-temperature PROX activity. Ru/YSZ can be easily oxidized and also reduced at low temperatures. It is found that Ru/YSZ uptakes only small amounts of CO₂, which can be desorbed at low temperatures. Ru/YSZ can reduce the high inlet CO concentration to be less than 10 ppm even in the presence of H₂O and CO₂.

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1. Introduction

Fuel cells, which can transform the chemical energy directly into the electricity, can be classified into various types depending on the kinds of electrolytes, operating temperatures and kinds of fuels [1]. Among them, the polymer electrolyte membrane fuel cell (PEMFC), in which the solid polymer is utilized as an electrolyte and whose operating temperature is relatively low compared with those of other types of fuel cells, has attracted much attention because of its high power density and easy start-up [2]. As a fuel for the PEMFC, hydrogen is currently produced from various fossil fuels through a series of chemical processes in which the steam reforming and the water–gas shift (WGS) are mainly involved. These two catalytic processes are thermodynamically limited and 0.5–1.0 vol.% of unconverted carbon monoxide remain in the hydrogen fuel downstream of the WGS reactor [2,3]. This residual CO should be controlled to be less than 10 ppm because the Pt-based anode of PEMFC can be poisoned by CO in a hydrogen stream

[2,3]. Therefore, the additional unit is needed to remove the residual CO in the H₂ generator for PEMFC. There are two representative catalytic ways to further remove CO after the water–gas shift reaction: the preferential CO oxidation (PROX) and the selective CO methanation. In the PROX system, the following two reactions mainly occur:



We need to find out the proper catalyst which can oxidize CO selectively in the presence of H₂ [3].

During the selective CO methanation, the following two hydrogenation reactions can be carried out at one time:



Therefore, the proper catalyst which is active for the CO methanation is highly required.

Until now, a number of catalysts for the PROX have been reported [4–39]. They can be grouped into non-noble metal oxides

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[4–6], supported Au catalysts [4,7], supported Pt catalysts [4,8–26] and supported Ru catalysts [8,23–39].

Unlike Pt-based catalysts, Ru-based catalysts have been reported to be active for the PROX as well as the CO methanation [40–45]. This can be beneficial for the CO removal in a H₂-rich stream as long as the selectivity for CO oxidation and CO methanation is high. In the case of Ru-based catalysts, the effect of kinds of Ru precursors, the preparation methods, the pretreatment conditions and kinds of a support on the PROX activity have been examined. Ruthenium nitrosyl nitrate has been reported to be the most plausible Ru precursor when supported Ru catalysts were prepared with an impregnation method [27,28]. In studies of the pretreatment condition, it was found that the supported Ru catalyst directly reduced with H₂ could show the higher PROX activity compared with those calcined in air and subsequently reduced in H₂ [28]. The additional pretreatment in a H₂/N₂ mixed gas flow was proposed to enhance the PROX activity for Ru/Al₂O₃ catalyst [34].

Until now, most PROX works have been conducted over Ru catalysts supported on Al₂O₃ [8,24–39] and SiO₂ [28]. In this work, we have examined the effect of support on the PROX activity over supported Ru catalysts to find an advanced catalyst which can remove the high inlet CO concentration to be less than 10 ppm over wide reaction temperature ranges through the selective CO oxidation and CO methanation.

2. Experimental

All the catalysts were prepared with a wet impregnation method from an aqueous solution of ruthenium nitrosyl nitrate (Ru(NO)(NO₃)₃·xH₂O, Aldrich). Various supports such as TiO₂ (Degussa, P-25, S_{BET} = 51.3 m²/g), yttria-stabilized zirconia (YSZ) (Tosoh, TZ-8Y, S_{BET} = 10.7 m²/g), SiO₂ (Aldrich, S_{BET} = 348.7 m²/g) and γ -alumina (Alfa, S_{BET} = 162.0 m²/g) were purchased and utilized.

ZrO₂ was prepared with a precipitation method. The pH of the aqueous solution of ZrCl₂O·8H₂O (Junsei) was increased to be 8 by adding 1 M NH₄OH solution. The slurry was aged at 353 K for 1 h, filtered and dried at 393 K overnight. Then, the solid product was calcined in air at 773 K.

The general procedure for the wet impregnation is as follows. Five grams of support was immersed in 50 ml of an aqueous Ru nitrosyl nitrate solution at 333 K for 6 h; the excess water was evaporated at 333 K in a rotary evaporator by controlling the pressure. The impregnated catalyst was further dried in air at 393 K overnight, and then the dried catalyst was reduced in H₂ at 573 K before a reaction.

The BET surface area was calculated from N₂ adsorption data that were obtained using an Autosorb-1 apparatus (Quantachrome) at liquid N₂ temperature. Before the measurement, the sample was degassed in vacuum for 4 h at 473 K. The results are listed in Table 1.

The Ru content of the prepared samples was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY-70Plus, Jobin-Yvon). The results are displayed in Table 1.

The CO chemisorptions were conducted in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD) to measure CO consumption. Quartz U-tube reactors were generally loaded with 0.2 g of sample, and catalysts were pretreated by reduction in H₂ at 573 K for 1 h, then cooled to room temperature. The CO chemisorptions were carried out at 300 K in 30 ml/min of He stream through a pulsed-chemisorptions technique, in which 500 μ l pulses of CO were utilized. In the case of Ru/YSZ after TPO experiment, the H₂-pretreatment at 573 K was not performed and 1.0 g of oxidized catalyst was utilized to try to measure the amount of chemisorbed CO more accurately. The CO chemisorptions results are listed in Table 1.

The CO₂ chemisorptions were conducted in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD) to measure CO₂ consumption. Quartz U-tube reactors were generally loaded with 0.2 g of sample, and catalysts were pretreated by reduction in H₂ at 573 K for 1 h, then cooled to room temperature. The CO₂ chemisorptions were carried out at 300 K in 30 ml/min of He stream through a pulsed-chemisorptions technique, in which 500 μ l pulses of CO₂ were utilized. The CO₂ chemisorptions results are presented in Table 1.

Temperature-programmed desorption (TPD) was conducted in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD) and an online mass spectrometer (QMS 200, Pfeiffer Vacuum) to detect any organic or inorganic species in the effluent stream during TPD experiment. Quartz U-tube reactors were generally loaded with 0.2 g of sample. The TPD was performed after CO₂ chemisorptions using 30 ml/min of He from 313 to 1073 K at a heating rate of 10 K/min after removing any weakly chemisorbed CO₂ in a line by flowing He at 313 K for 1 h.

Temperature-programmed oxidation (TPO) was conducted in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD) to measure O₂ consumption. A water trap composed of blue silica gel removed moisture from the TPO effluent stream at 273 K before the TCD. Quartz U-tube reactors were generally loaded with 0.2 g of sample, and catalysts were pretreated by reductions with H₂ at 573 K for 1 h, then cooled to room temperature. The TPO was performed using 30 ml/min of 2 vol.% O₂/He from 313 to 573 K at a heating rate of 10 K/min monitoring the thermal conductive detector (TCD) signals after removing any residual hydrogen in a line by flowing He at 313 K for 1 h.

Temperature-programmed reduction (TPR) was conducted on in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD) to measure H₂ consumption. A water trap composed of blue silica gel removed moisture from the TPR effluent stream at 273 K before the TCD. Quartz U-tube reactors were generally loaded with 0.2 g of sample. The TPR was

Table 1
The physicochemical properties of supported Ru catalysts.

Catalyst	Ru content ^a (wt.%)	Surface area ^b (m ² /g)	Amount of chemisorbed CO ^c (μ mol CO/g _{cat.})	[CO]/[Ru] ^c	Amount of chemisorbed CO ₂ ^d (μ mol CO ₂ /g _{cat.})
Ru/YSZ	0.64	12.3	25.4	0.40	5.5
Ru/ γ -Al ₂ O ₃	0.58	159.7	43.7	0.76	18.9
Ru/TiO ₂	0.64	53.8	39.4	0.62	3.9
Ru/SiO ₂	0.51	323.8	4.5	0.09	~0
Ru/ZrO ₂	0.60	68.5	77.8	1.31	116.9

^a The Ru content was determined with inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

^b The surface area was calculated with the BET method based on the N₂ physisorption data at liquid N₂ temperature.

^c The CO chemisorptions were measured at 300 K in He.

^d The CO₂ chemisorptions were measured at 300 K in He.

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