



Selective CO oxidation in a hydrogen-rich stream over Ru/SiO₂

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ABSTRACT

We prepared various Ru catalysts supported on silicas with different surface areas by an incipient wetness impregnation method and applied them in selective CO oxidation in a H₂-rich stream. For comparison, complete CO oxidation was also examined. The physical properties were probed with N₂ physisorption. The Ru dispersion was measured with CO chemisorption and transmission electron microscopy (TEM). The interaction between the catalyst surface and a reactant was examined with O₂ chemisorption, temperature-programmed oxidation (TPO), and temperature-programmed reduction (TPR). The BET surface area and total pore volume of the silica decreased with increasing calcination temperature. The average pore diameter of the silica increased with calcination temperature. The existence of micropores was not observed in the silica calcined in air at temperatures of 1103 K and above. The amount of CO and O₂ chemisorbed on Ru/SiO₂ at 300 K decreased with decreasing surface area of the silica. The particle size of Ru metal in Ru/SiO₂ generally increased with decreasing surface area of the silica. Ru/SiO₂ with a larger Ru particle size showed superior catalytic activities for the complete CO oxidation and the selective CO oxidation in a H₂-rich stream, compared to Ru/SiO₂ with a smaller Ru particle size, which might be due to the resistance to oxidation of Ru metal into RuO_x species. The Ru particle size also affects the fraction of active surface oxygen. Selected Ru/SiO₂ catalysts can reduce a high inlet CO concentration to less than 10 ppm even in the presence of H₂O and CO₂.

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1. Introduction

As concerns about energy and the environment grow, increasing attention has been paid to fuel cells that convert chemical energy directly into electricity. Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have specific merits, such as low operating temperatures, high power density, and easy start-up [1]. The prerequisite for a PEMFC coupled with an on-board reformer is to clean up the residual CO in a hydrogen-rich stream, because CO can degrade the electrochemical performance of the Pt-based anode of a PEMFC severely, even at ppm levels [2]. It is generally recommended that the CO concentration be controlled to less than 10 ppm [2,3]. There are two different catalytic approaches to remove the residual CO: preferential CO oxidation (PROX) and selective CO methanation [3]. During PROX, the following two reactions mainly occur:



During selective CO methanation, the following two hydrogenation reactions proceed:



Under actual conditions, PROX and selective CO methanation can occur at the same time because all of the reactants (CO, CO₂, and H₂) are present simultaneously. In all cases, selective catalyst activity for reactions (1) or (3) is required.

A large number of PROX catalysts have been reported, including non-noble metal oxides [4–6], Au-based catalysts [4,7–9] and Pt-based catalysts [4,10–23]. Ru-based catalysts have been reported to be active for PROX [10,21–39] as well as CO methanation [40–46].

Under the same PROX conditions, Ru/Al₂O₃ catalyst was selected as the most plausible candidate among the commercial noble metal catalysts [10,23]. In the case of Ru-based catalysts, factors on the PROX activity such as the nature of the Ru precursor, preparation methods, pretreatment conditions, and kinds of supports have been examined. When Ru-based catalysts were prepared by the impregnation method, it was reported that ruthenium nitrosyl nitrate is the most plausible precursor than other precursors such as ruthenium chloride and ruthenium carbonyl [24,25]. In terms of pretreatment conditions, supported Ru catalysts reduced

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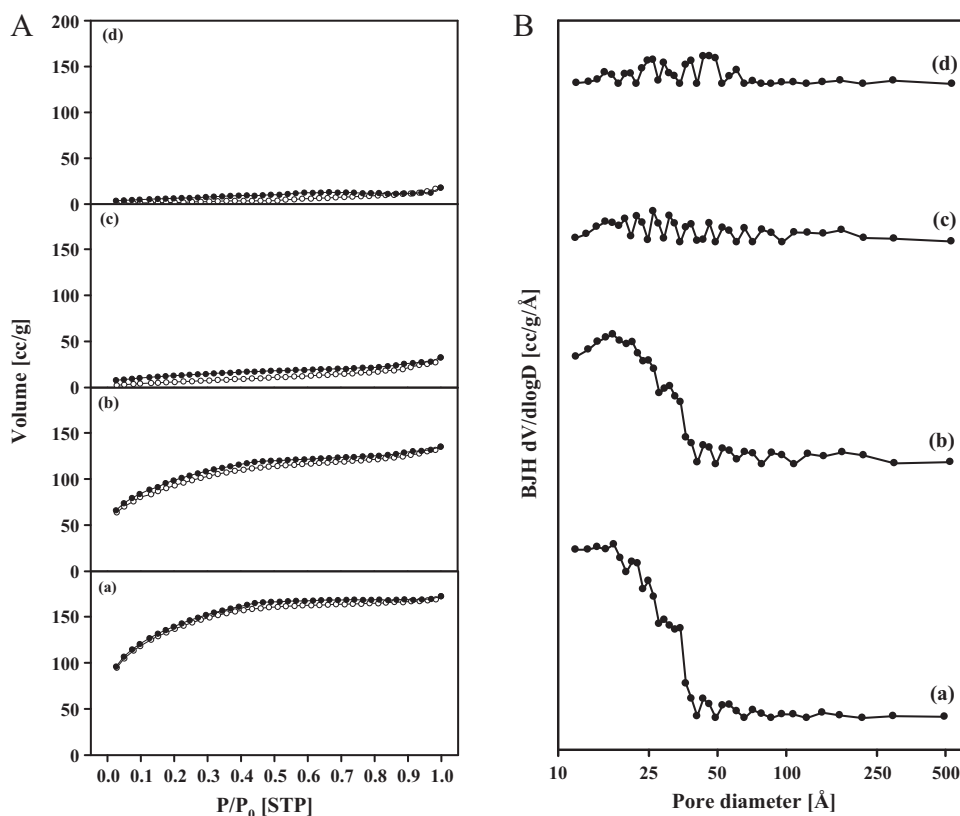


Fig. 1. (A) Nitrogen adsorption (unfilled points) and desorption (filled points) isotherms and (B) pore-size distribution plots for silicas prepared by calcination of silica gel at different temperatures, viz. (a) 973 K, (b) 1023 K, (c) 1103 K, and (d) 1123 K.

by H₂ without the calcination step showed the higher PROX activity compared with those calcined in air and subsequently reduced in H₂ [25].

Besides alumina and carbon, silica is a well-known support for supported metal catalysts. Although Ru/SiO₂ showed higher catalytic activity for this reaction than the Ru/Al₂O₃ catalyst [25,38], most studies have focused on Ru/Al₂O₃ [10,21–39]. In this study, we prepared various Ru/SiO₂ catalysts and investigated the main factors affecting their PROX activity.

2. Experimental

Various silica supports with different surface areas were prepared by calcination of silica gel (Sigma–Aldrich) in air at different temperatures, viz. 973 K, 1023 K, 1103 K, and 1123 K. To differentiate each support, the calcination temperature is denoted in parenthesis. All of the Ru/SiO₂ catalysts were prepared by an incipient wetness impregnation method. The Ru content was intended to be 1 wt.%. Ruthenium nitrosyl nitrate (Ru(NO)(NO₃)₃·xH₂O, Aldrich) was utilized as a ruthenium precursor. The catalyst, after drying in an oven at 393 K for 12 h, was reduced in a hydrogen stream at 573 K

without the calcination step. This catalyst preparation scheme has been proposed as the most effective one [25].

The physical properties of the support and the Ru catalyst were calculated from the N₂ adsorption/desorption data that were obtained using an Autosorb-1 apparatus (Quantachrome) at liquid N₂ temperature. Before the measurement, the sample was degassed under vacuum for 4 h at 473 K.

The amount of loaded Ru was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY-70 Plus, Jobin-Yvon).

The pulsed chemisorptions of CO and O₂ were conducted in an AutoChem 2910 unit (Micromeritics) equipped with a thermal conductivity detector (TCD) to measure the consumption of each gas. A quartz U-tube reactor was generally loaded with 0.20 g of the sample. All of the catalysts were reduced in H₂ at 573 K for 1 h, then cooled to room temperature. The chemisorptions were carried out at 300 K in a 30 ml/min stream of He using a pulsed-chemisorption technique, in which 500 μl pulses of each gas were utilized. Additionally, the pulsed chemisorptions of CO after exposure to 2 mol% O₂ in He at 373 K for 0.5 h were conducted in an AutoChem 2910 unit (Micromeritics). The products were analyzed by using a mass spectrometer (QMS 200, Pfeiffer Vacuum). In this case, the CO

Table 1
Physical properties of the various silica supports.

| Denoted SiO ₂ | BET surface area ^a (m ² /g) | Micropore surface area ^b (m ² /g) | External surface area ^b (m ² /g) | Micropore volume ^b (cm ³ /g) | Total pore volume (cm ³ /g) | Average pore diameter (nm) |
|---------------------------|--|--|---|---|---|-------------------------------|
| SiO ₂ (973 K) | 477.5 | 67.7 | 409.8 | 0.03 | 0.26 | 2.2 |
| SiO ₂ (1023 K) | 330.6 | 25.1 | 305.5 | 0.01 | 0.21 | 2.5 |
| SiO ₂ (1103 K) | 25.6 | – | 25.6 | – | 0.05 | 7.9 |
| SiO ₂ (1123 K) | 9.1 | – | 9.1 | – | 0.03 | 12.2 |

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

^b The data was obtained by the t-plot method [47].

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