



Highly active subnano Rh/Fe(OH)_x catalyst for preferential oxidation of CO in H₂-rich stream



Hongling Guan^{a,b}, Jian Lin^a, Lin Li^a, Xiaodong Wang^{a,*}, Tao Zhang^a

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 17 August 2015

Received in revised form

16 November 2015

Accepted 25 November 2015

Available online 27 November 2015

Keywords:

Rhodium

Fe(OH)_x

CO

Preferential oxidation

H₂

ABSTRACT

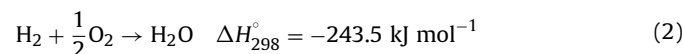
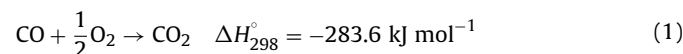
A novel catalyst formulation of 3.1 wt.% Rh/Fe(OH)_x was prepared via a co-precipitation method and investigated for CO preferential oxidation in H₂-rich stream. This catalyst exhibited a wider temperature range of 20–70 °C for CO total removal and better resistance to CO₂ and H₂O compared with the standard gold catalyst, standing out as the best Rh-based catalyst ever. The Rh species were highly dispersed in a subnano scale of ~1 nm and improved the reducibility of Fe(OH)_x support. The adsorption of O₂ was thus promoted over the reduced support, together with the weakened CO adsorption over the Rh clusters, permitting a non-competitive Langmuir–Hinshelwood mechanism through the elementary reaction of CO_(ad) + O_(ad). The reaction rate equation of $r = k[\text{CO}]^{0.73}[\text{O}_2]^{0.64}$ and small apparent activation energy of 24 kJ mol⁻¹ were then derived from the kinetic studies.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The preferential oxidation of CO in H₂-rich stream (PROX) (Eqs. (1) and (2)) has been considered as the most promising approach to eliminate CO from the hydrogen resource for proton-exchange membrane fuel cells (PEMFCs) [1–3]. The prerequisite for an efficient PROX catalyst is sufficiently high activity in the low-temperature oxidation of CO, even the selectively total removal of CO. Non-precious catalysts, especially the CuO/CeO₂, have attracted considerable interest from economical point of view with exceptional selectivity and stability [4–9]. It is now well recognized that the performances are related to the redox behavior with the interfacial interaction, and modifications such as the addition of heteroatoms are studied to improve their efficiency and stability [10]. Improvements are also observed with proper geometric type of the interacting surfaces [11] or the catalysts composition and morphology [12] are carried out to improve their efficiency and stability, but the total CO conversion temperatures are generally higher than 100 °C. Supported gold catalysts are well-known for their superior activity in room-temperature CO oxidation [13], while few of them are appropriate for the PROX reaction due to the competitive oxidation of H₂ at elevated temperatures, especially in the presence of H₂O and CO₂ [14–16]. Among various cata-

lysts developed, platinum group metal (PGM) based ones are the most intensively investigated and have been regarded as promising candidates, but the relatively high reaction temperatures (usually above 100 °C) seriously restrict their practical applications. In fact, due to the well-recognized significance of total CO removal at ambient temperatures for PEMFCs applications in transportation [3], endeavor efforts have been devoted to the design of highly active PROX catalysts, which still remains a formidable challenge.



Rhodium is one of the most widely used PGMs, especially for the mitigation of automotive exhaust pollutants [17–20]. The oxidation of CO by O₂, as an important constituent for that mitigation and a typical probe reaction in heterogeneous catalysis [21], has been extensively studied over various Rh-containing samples including single crystals [22,23], model nanoparticles [24,25], and supported catalysts [26–28]. Nevertheless, most of the studies were conducted under high temperature and vacuum conditions while less attention was paid to the low temperature regions. Particularly rare investigations have been performed for PROX reaction. In fact, there is no claiming for total CO removal at ambient temperature over Rh-based catalysts so far. Previous kinetic and mechanism studies of CO oxidation over Rh-based single crystals and Al₂O₃ or SiO₂ supported catalysts advocated a Langmuir–Hinshelwood

* Corresponding author. Fax: + 86 411 84685940.
E-mail address: xdwang@dicp.ac.cn (X. Wang).

(L–H) mechanism, of which the CO inhibition of the O₂ activation was recognized as the inherent reasons for the poor reactivity at low temperatures [22,29]. Accordingly, the weakening of CO adsorption and/or the promotion of O₂ activation should be an effective method to design efficient Rh-based catalysts for the low-temperature CO oxidation and PROX reaction.

Up to now, various PGM catalyst formulations for PROX have been developed in terms of promoting the activity of low-temperature CO oxidation. The Fe-containing materials, one of the most widely used reducible oxides, have been intensively studied as promoters for PROX since the seminal work of Korotkiikh and Farrauto [1,30]. Siani et al. suggested that the electronic interaction between Pt and Fe weakened the adsorption of CO on Pt, which in turn enhanced the rate of CO oxidation over PtFe/SiO₂ catalysts [31]. Kotobuki et al. ascribed the enhanced activity to the FeO_x species which strongly interacted with Pt and provided additional sites for O₂ adsorption over PtFe/mordenite catalyst [32]. Our group developed a promoted catalyst of IrFe/Al₂O₃ for PROX and proposed a bifunctional mechanism where the oxidation of CO occurred between CO on Ir sites and O₂ on FeO_x sites [33]. When we applied iron oxide directly as catalyst support, total CO conversion was realized at room temperature [34,35]. Similarly, Fu et al. accounted the superior PROX reactivity over FeO_x/Pt/SiO₂ catalyst for the interface-confined Fe²⁺ centers which not only weakened the CO adsorption but also facilitated the activation of O₂ [36]. Recently, with the results of DFT calculations and in situ DRIFTS experiments, Qiao et al. suggested that the weakened CO adsorption over Pt/FeO_x catalyst promoted the competitive adsorption of O₂, permitting mixture mechanisms of competitive and non-competitive/redox [37–39]. All the above cases highlighted the paramount role of O₂ activation and presented quotable reference for the fabrication of novel Rh-based catalyst for the efficient removal of CO. In this work, subnano Rh clusters were successfully prepared via a co-precipitation method with Fe(OH)_x as support. The derived Rh/Fe(OH)_x catalyst exhibited unprecedentedly high activity for PROX reaction with 100% CO conversion at a wide temperature range of 20–70 °C and good resistance to H₂O and CO₂. To our knowledge, it is the best Rh-based catalyst for PROX reported so far and even comparable with the standard gold catalyst. Detailed structure characterizations together with adsorption experiments and kinetic studies were conducted, with the traditional Rh/Al₂O₃ catalyst as comparison, to reveal the origin of its superior activity in the low temperature oxidation of CO.

2. Experimental

2.1. Catalyst preparation

Rh/Fe(OH)_x catalyst was prepared by co-precipitation method at a water-bath of 80 °C. In detail, an aqueous mixture of Fe(NO₃)₃·9H₂O (1 M) and RhCl₃·3H₂O (0.1 M) was added dropwise to a 0.2 M NaOH solution under stirring at 80 °C. The final pH was controlled around 8.5. After stirring reaction for 3 h and still ageing for 1 h, the mixture was filtered and washed with hot deionized water several times to remove salts, chloride and nitrate ions. Then the catalyst was dried overnight at 80 °C. Rh/Fe(OH)_x catalyst with nominal Rh loadings of 3.0 wt.% and 1.5 wt.% together with 3.0 wt.% Rh/Al₂O₃ catalyst were prepared with identical parameters. The actual loadings are 3.1 wt.%, 1.3 wt.% and 3.0 wt.%, respectively.

2.2. Activity test and kinetic studies

The catalytic activity was tested under atmospheric pressure in a fixed bed reactor with a U-shaped quartz tube of 10 mm inner diameter. Before evaluation, the Rh/Fe(OH)_x and Rh/Al₂O₃ catalysts

were subjected to a reduction pretreatment in a 20 mL min⁻¹ flow of 10 vol.% H₂/He at 200 °C (temperature ramp at 10 °C min⁻¹) for 30 min. The 4.4 wt.% Au/Fe₂O₃ standard catalyst provided by the World Gold Council (Au/Fe₂O₃–WGC, further information of the standard catalyst can be found in Supplementary information) was also tested for comparison with pretreatment at 200 °C in pure He. The PROX activity was measured in flow of 40 vol.% H₂ + 1 vol.% CO + 1 vol.% O₂ (30 mL min⁻¹, WHSV: 18,000 mL h⁻¹ g_{cat}⁻¹) and the catalyst bed was diluted with SiO₂. The effects of CO₂ (20 vol.%) and H₂O (3 or 10 vol.%) were also examined by bubbling the gas mixture through water at controlled temperatures. Stability tests were carried out at 80 °C with WHSV of 21,000 mL h⁻¹ g_{cat}⁻¹. The gas lines were heated at 120 °C to avoid water condensation on the lines. The gas composition was monitored by an on-line gas chromatograph (Agilent 6890, TDX-01 column, TCD detector) using He as carrier gas. The detection limit for CO was 10 ppm.

CO conversion (X_{CO}) was calculated as (Eq. (3)):

$$X_{CO} = \frac{n_{CO}^{in} - n_{CO}^{out}}{n_{CO}^{in}} \times 100\% \quad (3)$$

Selectivity to CO₂ (S_{CO_2}) was estimated from the oxygen mass balance as follows:

$$S_{CO_2} = \frac{n_{CO}^{in} - n_{CO}^{out}}{2(n_{O_2}^{in} - n_{O_2}^{out})} \times 100\% \quad (4)$$

The oxygen excess factor (λ) is defined as Eq. (5) and the value used herein was 2:

$$\lambda = 2 \times \frac{n_{O_2}^{in}}{n_{CO}^{in}} \quad (5)$$

For kinetic measurements, the conversions of all reactants were maintained below 20% by conditioning the space velocity. The CO conversions (X_{CO}) were used to calculate the CO oxidation rates (mol_{CO} g_{Rh}⁻¹ h⁻¹):

$$r_{CO} = \frac{X_{CO} \cdot N_{CO}}{m_{Rh}} \quad (6)$$

where m_{Rh} was the mass of rhodium in the reactor bed, N_{CO} was CO molar gas flow rate in mol h⁻¹. The reaction rates could be converted into turnover frequencies (TOF):

$$TOF = \frac{r_{CO} \cdot M_{Rh}}{D_{Rh}} \quad (7)$$

where M_{Rh} was the molar weight of Rh and D_{Rh} was the dispersion of Rh.

$$k = Ae^{-E_a/RT} \quad (8)$$

$$r_{CO} = kP_{CO}^{\alpha_{CO}} P_{O_2}^{\alpha_{O_2}} \quad (9)$$

$$\ln r_{CO} = \alpha_{CO} \ln P_{CO} + \ln(k \times P_{O_2}^{\alpha_{O_2}}) \quad (10)$$

$$\ln r_{CO} = \alpha_{O_2} \ln P_{O_2} + \ln(k \times P_{CO}^{\alpha_{CO}}) \quad (11)$$

The apparent activation energies (E_a) and reaction orders can be determined according to the Arrhenius equation in Eq. (8) and power rate law in Eq. (9). The CO reaction orders α_{CO} were derived from in Eq. (10) by taking logarithm both sides of Eq. (5) with variant P_{CO} and constant P_{O_2} . Similarly, O₂ reaction orders α_{O_2} could be obtained under constant P_{CO} and variant P_{O_2} from Eq. (11).

2.3. Catalyst characterization

The Rh loadings of the synthesized samples were determined using Thermo IRIS Intrepid II inductively coupled plasma (ICP) (Thermo Electron Corporation). The sample was dissolved with nitrohydrochloric acid.

Download English Version:

<https://daneshyari.com/en/article/6499378>

Download Persian Version:

<https://daneshyari.com/article/6499378>

[Daneshyari.com](https://daneshyari.com)