Remarkable effects of hydroxyl species on low-temperature CO (preferential) oxidation over Ir/Fe(OH)$_x$ catalyst

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ABSTRACT

Fe(OH)$_x$-supported noble metal catalysts exhibited good performance in low-temperature CO oxidation or CO preferential oxidation (PROX), which usually resulted from the high reducibility of Fe(OH)$_x$. However, we found here that the use of Fe(OH)$_x$ promoted the formation of OH species during PROX over Ir/Fe(OH)$_x$ catalysts, which not only greatly lowered the temperature for 100% CO conversion, even to room temperature, but also improved the stability. These OH species originated from the reaction between the adsorbed O on Fe^{2+} sites and the adsorbed H on Ir sites. They changed the reaction route for the oxidation of CO through adsorbed CO and OH with lower activation energy (E_a: ~5.2 kJ/mol) rather than through adsorbed CO and O (E_a: ~15.4 kJ/mol). With further time-resolved mass spectroscopy and diffuse reflectance infrared spectroscopy, the OH species, prior to the adsorbed O, were proved to react with CO directly.

1. Introduction

Low-temperature CO oxidation, a prototypical reaction in heterogeneous catalysis, is not only useful as a model reaction to fundamentally study the reaction mechanism or the nature of the catalysts, but also greatly important in many practical applications such as air cleaning and automotive emission control [1]. Recently, a special application, preferential oxidation of CO in H$_2$-rich gas (PROX), has aroused increasing attention due to its importance in purifying H$_2$ for the polymer electrolyte membrane fuel cell (PEMFC). The PEMFC is a potential power source for transport and portable applications. Nowadays, H$_2$ is mainly produced by the reforming of hydrocarbons; it usually contains small amounts of CO (0.5–1 vol%) even after high- and low-temperature water gas shift reactions (WGS) [2]. This amount of CO will poison the PEMFC anode catalyst and thus needs to be reduced to an acceptable level (below 100 ppm). Among the developed chemical or physical methods, PROX is considered as the lowest-cost and most effective one [3,4].

To date, various catalyst formulations have been developed for CO oxidation or PROX [5–7], especially reducible-oxide-supported noble metal catalysts [8–13]. The Fe-containing materials have

been extensively studied as one type of reducible oxides [14–16]. Siani et al. found that the FeO$_x$-promoted Pt/SiO$_2$ catalyst can decrease the temperature for CO total conversion by about 100 °C compared with the Pt/SiO$_2$ catalyst [17]. Goodwin et al. thought that FeO$_x$ interacted strongly with Pt and provided sites for O$_2$ adsorption over PtFe/Al$_2$O$_3$ [18]. We designed a bifunctional catalyst, IrFe/Al$_2$O$_3$, for PROX, over which the reaction between CO adsorbed on Ir sites and O$_2$ adsorbed on FeO$_x$ occurred [19]. Further quasi in situ ^{57}Fe Mössbauer spectroscopic study suggested that the activity of PROX increased with the amount of ferrous sites (Fe^{2+}), and Fe^{2+} was the site for oxygen adsorption [20]. Similarly, Fu et al. considered the interface-confined coordinatively unsaturated ferrous sites neighboring Pt as the active center for O$_2$ adsorption and activation [21]. All these works revealed that low-valence Fe sites are critical for CO oxidation and PROX. The special Fe(OH)$_x$, of which the Fe–O bond length is longer than in the traditional Fe$_2$O$_3$ [22], was easily reduced to form Fe^{2+} sites. The good reducibility usually explained the high activity of Fe(OH)$_x$-supported noble metals such as Au, Pd, and Pt catalysts for low-temperature CO oxidation [23–27].

However, besides good reducibility, Fe(OH)$_x$ is rich in surface OH species [9,28], the role of which should be considered in CO oxidation [29,30]. Smit et al. found that a large amount of OH species on low-temperature calcined iron oxide favored CO oxidation [31,32]. Huang et al. exposed the model FeO(1 1 1) to

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gas-phase atomic deuterium (D) or water to fabricate surface-adsorbed OH species and found that it reacted readily with CO adsorbed onto Pt(1 1 1) [33,34]. With the consumption of surface OH species, the catalyst performance decreased. We recently proposed that the reaction between adsorbed O and H to form OH species was the rate-limiting step for PROX over the IrFe/SiO$_2$ catalyst, based on a microkinetic model [35]. All these results implied that the formation and maintenance of OH species could be necessary to obtain a catalyst with high activity for CO oxidation and PROX. Moreover, the OH species that come from humidity or are generated as intermediates are inevitable for both CO oxidation and PROX in practical applications. Therefore, to make clear the effect of OH species in CO oxidation/PROX is highly desirable. Nevertheless, this effect on the performance of Fe(OH)$_x$-supported noble metal catalysts in CO oxidation/PROX has not been reported in detail.

Previously, we prepared a novel Ir/Fe(OH)$_x$ catalyst that exhibited activity comparable to that of the standard Au/Fe$_2$O$_3$ catalyst. It was found that the strong interaction between Ir and Fe(OH)$_x$ promoted the reduction of Fe(OH)$_x$ to form Fe^{2+}, which promoted the adsorption of O$_2$ [36]. Here, we present a detailed study through a series of characterizations including microcalorimetry, in situ DRIFTS, and time-resolved CO titration. These characterizations, together with the reaction data, unequivocally suggest that the OH species generated from the reaction between H$_2$ and O$_2$ or between H$_2$O and O$_2$ is critical for the good performance of Ir/Fe(OH)$_x$ catalyst in CO oxidation and PROX. The OH species changed the reaction routes for the oxidation of CO and significantly improved the activity and stability of the Ir/Fe(OH)$_x$ catalyst.

2. Experimental

2.1. Catalyst preparation

The Ir/Fe(OH)$_x$ catalyst was prepared by a co-precipitation method as reported previously [36]. In detail, an aqueous mixture of H$_2$IrCl$_6$ and Fe(NO$_3$)$_3$ was added to NaOH solution under strong stirring at 80 °C. The final pH of the solution was controlled around 8. After stirring for 3 h and aging for 1 h, the suspension was filtrated and washed with hot distilled water several times. The sample dried at 80 °C overnight was denoted as Ir/Fe-UC, while those further calcined at 200 and 400 °C for 6 h were denoted as Ir/Fe-C2 and Ir/Fe-C4, respectively.

2.2. Activity test

Catalytic performance was evaluated in a fixed-bed reactor at atmospheric pressure with 100 mg catalyst. Prior to the test, the catalysts were reduced in situ with 10 vol% H$_2$/He at 200 °C for 30 min. After the catalysts cooled to room temperature, feed gases containing 1 vol% CO, 1 vol% O$_2$, and different percentages of H$_2$ balanced with He passed through the reactor at a space velocity of 18,000 mL h^{-1} g$_{cat}^{-1}$. In some cases the water was added by a bubble method. The effluent gas was analyzed by an online gas chromatograph (Agilent 6890, TDX-01 column). CO$_2$ and H$_2$O were detected as the only products.

CO conversion (X_{CO}) is calculated as

$$X_{CO} = \frac{n_{CO}^{in} - n_{CO}^{out}}{n_{CO}^{in}} \times 100 \ (\%), \tag{1}$$

where n_{CO}^{in} and n_{CO}^{out} represent the inlet and outlet amounts of CO (μmol), respectively.

Specific reaction rates and TOF of Ir/Fe(OH)$_x$ under CO oxidation and PROX conditions at different temperatures were obtained by keeping the CO conversions below 20%. Toward this goal, a certain amount of the sample was diluted with 100 mg SiC. For each run at a specified reaction temperature, the CO conversions at 20, 40, and 60 min were averaged and used to calculate specific rates to acquire the data for an Arrhenius curve. The TOF values were given based on the dispersions from CO chemisorption.

2.3. ICP, BET, H$_2$ TPR, XPS, and FT-IR

The actual Ir loadings of the Ir/Fe-UC, Ir/Fe-C2, and Ir/Fe-C4 samples were determined by inductively coupled plasma (ICP) spectroscopy on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The Brunauer–Emmett–Teller (BET) surface areas of these catalysts were measured by nitrogen adsorption at −196 °C using a Micromeritics ASAP 2010 apparatus.

Temperature-programmed reduction of hydrogen (H$_2$ TPR) was performed on an Auto Chem II 2920 apparatus. Prior to the measurement, the catalyst sample was pretreated in Ar flow at 120 °C for 2 h. After the sample cooled to room temperature, the gas flow was switched to 10 vol% H$_2$/Ar and the sample was heated to 900 °C with a temperature ramp of 10 °C min^{-1}.

X-ray photoelectron spectra (XPS) were determined on a VG ESCALAB 210 apparatus to obtain the surface compositions and the binding energies of the catalysts. Mg $K\alpha$ radiation at an energy scale calibrated versus adventitious carbon (C1s peak at 284.5 eV) was used. The samples were prereduced at 200 °C before the characterization.

Fourier transform infrared spectroscopy (FT-IR) studies were performed in a transmission mode with a BRUKER Equinox 55 spectrometer at a resolution of 4 cm^{-1} to detect the species in the samples. The fresh samples Ir/Fe-UC, Ir/Fe-C2, and Ir/Fe-C4 and the reduced ones were measured at room temperature and atmospheric pressure.

2.4. O$_2$ adsorption microcalorimetry, in situ DRIFTS, and CO titrations

O$_2$ adsorption microcalorimetric measurements were performed at 40 °C using a BT 2.15 heat-flux calorimeter (Setaram, France), which has been described in detail earlier [37]. The calorimeter was connected to a gas-handling and a volumetric system employing MKS 698A Baratron capacitance manometers for precision pressure measurement (±1.33 × 10^{-2} Pa). Prior to the characterization, the samples Ir/Fe-UC, Ir/Fe-C2, and Ir/Fe-C4 were prereduced by H$_2$ at 200 °C and then evacuated at 210 °C. These samples were transferred to a side-armed Pyrex and sealed in a Pyrex capsule, which can minimize possible contamination in the high vacuum system in the course of thermal equilibration (6–8 h) with the calorimeter. After thermal equilibrium was reached, the capsule was broken by a vacuum feedthrough and the fresh catalyst was exposed. The microcalorimetric data were then collected by sequentially introducing small doses (1–10 μmol) of O$_2$ onto the sample until it became saturated (5–6 Torr). The differential heat versus adsorbate coverage plots and adsorption isothermals were obtained simultaneously.

In situ diffuse reflectance infrared spectroscopy (DRIFTS) spectra were also acquired with a BRUKER Equinox 55 spectrometer equipped with a MCT detector and operated at a resolution of 4 cm^{-1}. Before each experiment, a 40 mg sample was reduced in situ at 200 °C for 1 h. After the sample cooled to the desired temperature, the gas for adsorption (CO, CO oxidation, and PROX mixture) was introduced into the reaction cell at a total flow rate of 100 mL min^{-1}. The spectra were recorded as a function of the time on stream against a background of the sample at the desired temperature under flowing He.

Time-resolved CO titrations were carried out by online mass spectroscopy (MS) analysis. The gate time for analysis was 0.1 s for each detected component (CO, O$_2$, CO$_2$, He, H$_2$O), equivalent to the acquisition of two data points per second. Typically, a