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Versatile application of wet-oxidation for ambient CO abatement over $\text{Fe}(\text{OH})_x$ supported subnanometer platinum group metal catalysts

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ABSTRACT

The efficient and stable abatement of CO pollutant under ambient conditions is of great significance; however, it remains a formidable challenge. Herein, we report the versatile application of wet oxidation over $\text{Fe}(\text{OH})_x$ supported subnanometer Pt group metal (PGM) catalysts for the complete removal of CO under ambient temperature and humidity conditions. Typically, the 1.8 wt% Rh/ $\text{Fe}(\text{OH})_x$ catalyst exhibited better durability during a ~1400 min run for wet oxidation than for dry CO oxidation. Multiple characterization results including HR-TEM, H_2 -TPR, and in-situ DRIFTS suggested that $\text{Fe}(\text{OH})_x$, with good reducibility, promoted by the subnanometer Rh clusters, provided sites for the adsorption and reaction of O_2 and H_2O to form OH species. Subsequently, these OH species reacted with the adsorbed CO on Rh sites with a considerably lower activation energy (9 kJ mol⁻¹) than that of dissociated O species (22 kJ mol⁻¹), thus rationalizing the outstanding performance of Rh/ $\text{Fe}(\text{OH})_x$ for wet oxidation. Extended experiments with other PGMs revealed a good generality for the application of wet oxidation in the efficient abatement of CO under humid conditions with $\text{Fe}(\text{OH})_x$ as the support.

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1. Introduction

CO is one of the most widespread lethal pollutants from industrial and automobile exhaust emissions. Exposure to a small amount of CO can lead to serious toxic effects due to its ability

to strongly and rapidly bind to blood hemoglobin, which would block oxygen transport and cellular respiration. This is most liable to occur in enclosed spaces, such as mines, dwellings, food storage facilities, submarines, and orbital stations [1,2]. In addition, CO is well-known in many H_2 -involved industrial

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processes due to its poisoning action against the catalysts involved, including the Pt-based anode catalysts employed in polymer electrolyte membrane fuel cells (PEMFCs) and the Fe-based catalysts utilized for the synthesis of NH_3 [3]. Therefore, the mitigation of the CO concentration to a desirable level by catalytic oxidation ($2\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$), which is recognized as the most cost-effective solution for emission control and industrial hydrogen purification, has been widely studied in heterogeneous catalysis, photocatalysis, and electrocatalysis as a prototypical reaction [4,5].

Considering the required CO removal efficiency and ubiquitous water gas in many practical circumstances, the key issue associated with practical CO oxidation is the design of moisture-tolerable catalytic materials with substantially high catalytic activities at room or even lower temperatures [5–10]. Non-precious catalysts with improved oxygen mobilities and exceptional stabilities have attracted considerable interest from an economic point of view; however, the total CO conversion temperatures are generally higher than 100 °C [11–13]. Oxide catalysts including hopcalite (Cu-Mn-O_x) [14] and Co_3O_4 [15–18] catalysts are very active at or below room temperature, although moisture deactivates them rapidly. Supported gold catalysts are also highly active for CO oxidation, as total conversion can be achieved at sub-ambient temperatures [19]. However, the catalyst reproduction process requires further improvement due to the high sensitivity of the preparation and storage details [20,21], support property [22,23], particle size [24,25], and oxidation state of gold [26]. These limitations hinder their practical applications; consequently, versatile catalytic systems are urgently required.

The Pt group metal (PGM) based catalysts have been studied for almost a century since the pioneering work of Langmuir et al. [27]. In fact, to date, the commercial catalysts developed for exhaust gas treatments are mostly based on Pt-group elements due to their relatively high stability and excellent resistance to moisture [28]. They are very effective for CO abatement at temperatures above 200 °C; however, they provide limited reactivity at lower temperatures due to the poisoning effect of the strongly adsorbed CO on PGM sites [5]. This inevitably limits their practical applications, including the indoor air cleaning, the purification of industrial H_2 resource, as well as the control of the cold start emissions of automobile engines. Various aspects including the particle size [29], metal-support interfaces [30–32], bimetallic structures [33], and promoters [34] have been exploited to promote the O_2 activation and/or weaken the CO adsorption. Despite the significant advances [5,6,35], there is still no versatile strategy for the practical relevant ambient CO abatement over a PGM-promoted catalytic reaction system.

Although an intricate debate on the active sites and reaction mechanism is still on, iron oxides with rich OH groups have aroused extensive interests. Wagner et al. [36] prepared a variety of gold catalysts supported on iron oxides with variable proportions of ferrihydrite, haematite, and goethite, over which a positive correlation between the CO oxidation activity and FeOOH amount was revealed. Hutchings et al. [37] proposed that the most active state for the Au/FeO_x catalysts was com-

prised of poorly crystallized ferrihydrite. Similarly, Li et al. [38] suggested that the high performance of Fe_2O_3 nanoparticles in CO oxidation was attributed to the presence of a nanosized (3 nm) hydroxylated iron oxide phase. Deng et al. [39] proposed that the longer Fe–O bond of Fe(OH)_x support, compared to that of traditional Fe_2O_3 , facilitated its reduction and the activation of O_2 . Our group found that the good reducibility and rich OH groups of the Fe(OH)_x support could facilitate the dispersion of PGM species and stabilize them as subnanometer clusters or even single atoms [29]. However, the conversion rates for CO oxidation at ambient temperature are still far from satisfactory. In addition, the moisture effect as well as its participation pathways and mechanism in practical environments are still controversial and requires systematic investigations [9,10,40–44].

Previously, we synthesized a novel Fe(OH)_x supported subnanometer Rh catalyst, which performed total CO conversion over a wide working temperature window of 20–70 °C for the preferential oxidation of CO in a H_2 -rich stream. The subnanometer Rh clusters weakened the adsorption of CO and promoted the reduction of Fe(OH)_x for the adsorption of O_2 to permit a non-competitive Langmuir–Hinshelwood reaction: $\text{CO}_{(\text{ad})} + \text{O}_{(\text{ad})}$ [45]. Herein, as a typical example for the wet oxidation of CO under ambient conditions, we found, using a similar catalyst, that the adsorbed O species can facilely react with the H_2O on Fe(OH)_x to form hydroxyl species, which reacted with CO to produce CO_2 at a relatively high rate, but low activation energy. Such a proposed mechanism can be extended to other PGM-based catalysts, such as Ir and Pt, thus presenting a quotable reference for the efficient removal of CO under ambient conditions.

2. Experimental

2.1. Catalyst preparation

The Rh/Fe(OH)_x catalyst with a nominal loading of 2.0 wt% was prepared by co-precipitation method in an 80 °C water bath, as reported previously [45]. Typically, an aqueous mixture of $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.0 mol L^{-1}) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.1 mol L^{-1}) was added dropwise to a 0.2 mol L^{-1} NaOH solution under stirring at 80 °C. The final pH was maintained at ~8.5. After stirring for 3 h and ageing for 1 h, the mixture was filtered and washed with hot deionized water several times to remove salts, chloride, and nitrate impurities. Thereafter, the catalyst was dried overnight at 80 °C. The other Fe(OH)_x supported PGM catalysts including Ir- and Pt-based catalysts were prepared by a similar method.

2.2. Catalytic performance test

The catalytic activity was tested under atmospheric pressure in a fixed bed reactor with a U-shaped quartz tube having an inner diameter of 10 mm. Prior to the evaluation, the catalysts were subjected to a reduction pretreatment in a 20 mL min^{-1} flow of 10 vol% H_2/He at 200 °C (temperature ramp at 10 °C min^{-1}) for 30 min and flushed with He until cooling to the

desired temperature. For wet oxidation, 0.6 vol% H₂O was added by bubbling the CO oxidation gas mixture (1 vol.% CO + 1 vol.% O₂) through an ice bath at a weight hourly space velocity (WHSV) of 18,000 mL h⁻¹ g_{cat}⁻¹. The catalyst was diluted with SiO₂, and the gas lines were heated at 120 °C to avoid H₂O condensation on the lines. The gas composition was monitored using an on-line gas chromatograph (Agilent 7890, TDX-01 column, TCD detector) with He as the carrier gas. The detection limit for CO was 10 ppm.

The practical removal of a small amount of CO was simulated using a trace gas analyzer (Horiba VA-3000). The detection was carried out at 20 °C with a gas composition of 100 ppm CO + 20 vol% O₂ + 0.6 vol% H₂O at a considerably high WHSV of 120,000 mL h⁻¹ g_{cat}⁻¹. The CO concentration was recorded every 20 min with a measurement accuracy of ±1.0% F.S.

The CO conversions (X_{CO}) were calculated using Eq. (1):

$$X_{CO} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100\% \quad (1)$$

For the measurements of specific reaction rates (r_{CO}) and apparent activation energies (E_a), the conversions of all the reactants were maintained below 15% by conditioning the space velocity. For each run at a specific reaction temperature, the CO conversions at 20, 40, and 60 min were averaged and used to calculate r_{CO} :

$$r_{CO} = \frac{X_{CO} \cdot N_{CO}}{m_{Rh}} \quad (2)$$

where m_{Rh} is the mass of Rh in the reactor bed, and N_{CO} is the CO molar gas flow rate in mol h⁻¹.

E_a can be determined according to the Arrhenius equation in Eq. (3):

$$k = Ae^{-E_a/RT} \quad (3)$$

$$r_{CO} = kP_{CO}^{\alpha_{CO}}P_{O_2}^{\alpha_{O_2}} \quad (4)$$

where k is the reaction rate constant, which is proportional to r_{CO} at a constant gas feed composition, according to Eq. (4).

2.3. Catalyst characterization

The Rh loadings of the catalyst samples were determined by the Thermo IRIS Intrepid II inductively coupled plasma (ICP) technique after dissolution with nitrohydrochloric acid. The Brunauer–Emmett–Teller (BET) surface areas were measured using a Micromeritics ASAP 2010 apparatus. The experiment was carried out at -196 °C by nitrogen adsorption after the evacuation at 120 °C.

High-resolution transmission electron microscopy (HR-TEM) and high-angle annual dark-field scanning transmission electron microscopic (HAADF-STEM) observations were conducted on a JEOL (JEM-2100F) microscope. The samples were pre-reduced in 10 vol% H₂/He at 200 °C. Droplets of an ultrasonically dispersed ethanol suspension were deposited on a copper grid and dried in air.

X-ray diffraction (XRD) experiments were performed on a PW3040/60 X'Pert PRO (PANalytical) diffractometer equipped with a monochromatized Cu $K\alpha$ radiation source ($\lambda = 0.15432$ nm), operating at 40 kV and 40 mA at a scanning speed of 10° min⁻¹.

In-situ IR experiments were conducted in a diffuse reflectance (DRIFTS) mode using a Bruker EQUINOX 55 spectrometer, equipped with an MCT detector and operated at a resolution of 4 cm⁻¹ for 64 scans. Prior to each experiment, the sample (~20 mg) was reduced in-situ in 10 vol% H₂/He at 200 °C in a DRIFTS cell (HC-500, Pike technologies). Subsequently, the temperature was reduced to 80 °C and maintained for 30 min under flowing He. Thereafter, a background spectrum was recorded, which was then subtracted automatically from the subsequent spectra. Afterward, the corresponding feed gas for the adsorption was introduced, and the spectrum was recorded as a function of time until saturation. The rate of all the flows involved was 30 mL min⁻¹.

Time-resolved CO-titration IR experiments were carried out at 80 °C after the introduction of CO onto the catalysts pretreated by O₂ and H₂O. Prior to each experiment, the sample (~20 mg) was reduced in-situ in 10 vol% H₂/He at 200 °C. The flow of the O₂ + H₂O gas was firstly coadsorbed over this sample and subsequently flushed with He. Using this as the background, the catalyst was assumed to be rich in OH species. A flow of CO (30 mL min⁻¹) was subsequently introduced. The changes of multiple peaks attributed to CO, CO₂, OH, and formates were recorded as a function of time.

3. Results and discussion

The physiochemical properties including the Rh loading and BET surface areas were investigated. It was found that the Rh loadings were approximately 1.8 wt% and 2.0 wt% when Fe(OH)_x and Al₂O₃ supports were employed, respectively. Moreover, the BET surface areas were also approximately 300 m² g⁻¹ for both Rh/Fe(OH)_x and Rh/Al₂O₃ supports, which is exclusive of their influence on the catalytic performance.

3.1. Catalytic performance: Effect of H₂O

Fig. 1 presents the profiles of the CO conversion over Rh/Fe(OH)_x and Rh/Al₂O₃ catalysts as a function of the reaction temperature. Complete CO conversion (100%) was achieved over the Rh/Fe(OH)_x catalyst even at 20 °C for wet oxidation, which implies that we obtained a highly active catalyst for the complete CO elimination under ambient temperature and humidity conditions. In the absence of H₂O, however, the CO oxidation activity was considerably reduced; the CO conversion was only 36% at 20 °C and 92% at 100 °C. The first decrease and subsequent increase in the CO conversion with the reaction temperature resulted from the consumption of surface OH groups over Fe(OH)_x, which will be further demonstrated by stability tests and in-situ DRIFTS characterization. This result suggests that H₂O has a significant promotional effect on the CO oxidation activity over Rh/Fe(OH)_x. The Rh/Al₂O₃ catalyst was also investigated as a reference. Interestingly, H₂O has a slight effect on this catalyst toward the CO oxidation, considering that negligible CO conversion was achieved at ambient temperature and only 30% at 100 °C. This suggests that the activity of Rh-based catalysts and the contribution role of H₂O are dependent on the type of support. The significant promotional

Fig. 1. (a) CO conversions over Rh/Fe(OH)_x and Rh/Al₂O₃ catalysts for wet oxidation as a function of the reaction temperatures. Reaction conditions: 1 vol% CO, 1 vol% O₂, (0.6 vol% H₂O) and balance He. WHSV=18,000 mL g_{cat}⁻¹ h⁻¹.

effect can be achieved when Fe(OH)_x is used as support rather than the inert Al₂O₃.

To compare the intrinsic activities, the specific reaction rates over Rh/Fe(OH)_x at 27 °C and Rh/Al₂O₃ at 60 °C were tested and are illustrated in Fig. 2. The reaction rate for the CO oxidation over Rh/Fe(OH)_x was 0.09 mol_{CO} g_{Rh}⁻¹ h⁻¹, while it was increased by 5 times to 0.45 mol_{CO} g_{Rh}⁻¹ h⁻¹ after the addition of H₂O. For the Rh/Al₂O₃ catalyst, the reaction rate at 60 °C was only 0.034 mol_{CO} g_{Rh}⁻¹ h⁻¹. The addition of H₂O exerted almost no influence on this rate as a similar value of 0.037 mol_{CO} g_{Rh}⁻¹ h⁻¹ was obtained. These results indicate the indispensable role of the Fe(OH)_x support in the promotional effect of H₂O.

For many CO oxidation catalysts, poor stability under humid conditions is the most universal drawback associated with

Fig. 2. Specific reaction rates over Rh/Fe(OH)_x at 27 °C and Rh/Al₂O₃ at 60 °C. For CO+O₂, 14.6 mg of Rh/Fe(OH)_x and 28.1 mg of Rh/Al₂O₃ were exposed to the reactant at flow rates of 30 and 20 mL min⁻¹, respectively. For CO+O₂+H₂O, 11.4 mg of Rh/Fe(OH)_x and 70 mg of Rh/Al₂O₃ were exposed to the reactant at flow rates of 45 and 20 mL min⁻¹, respectively.

practical applications. Consequently, we investigated the effect of H₂O on the long-term run of CO oxidation over the Rh/Fe(OH)_x catalyst. The original CO conversion was maintained lower than 100% by increasing the space velocity. As shown in Fig. 3, excellent stability was achieved with a CO conversion of around 75% for a ~1400 min run during the wet oxidation process. Comparatively, for the CO oxidation without H₂O, the CO conversions decreased almost linearly from ~54% to ~30% after a 100 min run, and thereafter, gradually to ~10% after a 1060 min run. This is probably owing to the consumption of the surface OH groups of Fe(OH)_x and the accumulation of carbonates [46]. Therefore, the presence of H₂O not only enhances the catalyst efficiency but also improves the stability.

The abatement of small amounts of CO at ambient temperature was further simulated using a trace gas analyzer. As shown in Fig. 4, the CO concentration decreased sharply to around 4 ppm from the original value of 100 ppm. Afterward, the value remained constant with the time on stream under an extremely high space velocity of 120,000 mL g_{cat}⁻¹ h⁻¹ during the whole test period, which is much lower than the stipulated CO concentration for life safety (< 24 ppm) and tolerance limit of the Pt-anode of PEMFCs (< 10 ppm) [5]. These results suggest that the Rh/Fe(OH)_x catalyst can fulfill the mandatory requirements for the control of the CO concentration in most domestic and industrial applications.

3.2. Factors for high performance during wet oxidation

3.2.1. Dispersion of subnanometer Rh species on Fe(OH)_x

HR-TEM and HAADF-STEM techniques were employed to visualize the dispersion and configuration of the catalysts. As shown in Fig. 5(a), lattice fringes with spacing values of 0.242 and 0.251 nm, corresponding to the (222) and (311) planes of Fe₃O₄, respectively, can be clearly observed, indicating the reduction of the Fe(OH)_x support to Fe₃O₄ during H₂ treatment. Meanwhile, the Rh species exist as small clusters with an average particle size of 0.9 nm, as can be observed in Fig. 5(b). In

Fig. 3. Stability results of the CO oxidation over the 1.8 wt% Rh/Fe(OH)_x catalyst at 40 °C. Reaction conditions: 1 vol% CO + 1 vol% O₂, (0.6 vol% H₂O) and balance He. WHSV = 36,000 mL g_{cat}⁻¹ h⁻¹.

Fig. 4. Simulation of the practical removal of a small amount of CO at 20 °C. Reaction conditions: 100 ppm CO + 20 vol% O₂ and 0.6 vol% H₂O. WHSV = 120,000 mL g_{cat}⁻¹ h⁻¹.

other words, the subnanometer Rh clusters were highly dispersed on Fe₃O₄. This phenomenon was also found on other Fe(OH)_x supported noble metal catalysts: that the co-precipitation method can afford catalysts with dominant subnanometer metal clusters and a small number of single atoms when the metal loading amount is higher than 2 wt% [47,48]. For comparison, we investigated the Rh/Al₂O₃ catalyst with a similar Rh loading. As shown in Figs. 5(c) and 5(d), the Rh species were dispersed as nanoparticles with an average size of 1.6 nm, which is slightly higher than that of Rh/Fe(OH)_x. These results suggest that the Fe(OH)_x support plays an important role in the dispersion and stabilization of the Rh subnanometer clusters, probably related to the defect sites of the reducible support.

3.2.2. In-situ DRIFTS studies during the wet oxidation of CO

Fig. 5. Typical HR-TEM/HAADF-STEM images and size distributions of Rh/Fe(OH)_x (a,b) and Rh/Al₂O₃ (c,d).

The catalytic performance measurements suggest that the presence of H₂O had a great promotional effect on the CO oxidation over Rh/Fe(OH)_x, which is required for its activity and stability at ambient temperatures. Subsequently, the in-situ DRIFTS measurements were employed to investigate the effect of H₂O on the adsorption and reaction behaviors during the wet oxidation of CO. As shown in Fig. 6, after CO adsorption, only the doublet peaks of gem-carbonyl species [Rh^I(CO)₂] (2088 and 2018 cm⁻¹) without linear and bridged (~2060 and ~1860 cm⁻¹, respectively) ones were observed, indicating the high dispersion of Rh species with a positive charge [49,50]. After the addition of O₂, the wavenumbers of the CO adsorption peaks remained constant, implying that O₂ was adsorbed on the support, and the chemical state of Rh remained unchanged. With the further addition of H₂O, there was still no change in the CO adsorption peaks. These results suggest that the Fe(OH)_x support plays a crucial role in the adsorption of both O₂ and H₂O, and there is no competition for the adsorption of CO between O₂ or H₂O on Rh/Fe(OH)_x. Moreover, the strong peaks at around 3600–3000 and 1630 cm⁻¹, which are attributed to OH groups, appeared and increased with the reaction time. The bands between 2400 and 2300 cm⁻¹, attributed to the gaseous CO₂, increase greatly, coupled with those of formate or carboxyl species at 1530 and 1438 cm⁻¹ [51,52], indicating the promotional effect of the OH species on the CO conversion. The promotional effect of H₂O in the form of OH species on the supported metal catalyst for CO oxidation has been studied on Pt₁/CeO₂ catalyst by DFT calculations [53]. It was suggested that an MvK-type reaction mechanism occurred, i.e., CO on Pt₁ sites react with the OH from the dissociated H₂O on Ce sites to yield a carboxyl intermediate, which then dehydrogenates with another OH to produce CO₂ and H₂O. Similarly, in our work, the adsorption of H₂O occurred mainly on the support in view of the absence of a CO peak shift with the addition of H₂O, as shown in the inset of Fig. 6. The H₂O could react with the dissociated O on the support to form OH species, which

Fig. 6. In-situ DRIFTS spectra of the effect of H₂O addition on the CO oxidation with time on stream, over the Rh/Fe(OH)_x catalyst, at 80 °C. The inset figure shows the change of the CO adsorption peaks under different conditions.

then react with the adsorbed CO on Rh sites to form CO₂.

3.3. Discussion

The catalytic oxidation of CO is generally regarded as one of the most effective routes for decreasing the concentration of CO emissions. However, the catalyst performance at ambient temperature still requires improvements. Particularly, the effect of humidity should be considered due to its ubiquity in many circumstances. Here, we found that the subnanometer Rh/Fe(OH)_x catalyst can work well for practical CO abatement via wet oxidation. The ambient humidity condition not only greatly decreases the temperature required for the complete CO removal to 20 °C, but also improves the stability of Rh/Fe(OH)_x (Figs. 1–3). Comparatively, the CO conversions at ambient temperatures are still limited to less than 40% in the absence of water, although it has been found, previously, that the CO adsorption is weakened over the subnanometer Rh clusters, and the formation of oxygen vacancies on Fe(OH)_x could greatly facilitate the activation of O₂ [45]. These results suggest that the weakened CO adsorption on the subnanometer metal sites and the facile O₂ activation on the reduced oxide may be required; however, they are not sufficient for the total CO conversion at ambient temperatures.

On the other hand, the OH species have been suggested to have remarkable effects on the CO oxidation. Chandler et al. [42] suggested that there was no direct involvement of OH groups in the reaction mechanism and that their function was only to stabilize the H₂O species near the Au/TiO₂ interface. In contrast, Mullins et al. [43] provided direct evidence with oxygen isotope labeling to track the reactive species on Au(111), which shows that CO₂ was produced from the CO reaction with both the chemisorbed “atomic” oxygen and OH groups. Huang et al. [41] designed a model FeO(111)/Pt(111) catalyst with surface OH species, on which the performance of CO oxidation decreased with the consumption of surface OH species. On our Rh/Fe(OH)_x catalyst, the OH groups were formed from the reaction between adsorbed H₂O and O species on Fe(OH)_x, as shown in the DRIFTS results in Fig. 6. These OH species can

Fig. 7. Arrhenius plot of $\ln r_{\text{CO}}$ versus $1000/T$ for the CO oxidation over the Rh/Fe(OH)_x catalyst as a function of the reaction temperatures. Reaction conditions: 1 vol% CO + 1 vol% O₂, with or without 0.6 vol% H₂O, and balance He. WHSV was adjusted to ensure CO conversions below 15%. For CO+O₂, 14.6, 46.3, 13.3, and 21.8 mg of Rh/Fe(OH)_x, at reactant flow rates of 30, 60, 60, and 60 mL min⁻¹, were detected at 27, 40, 60, and 80 °C, respectively. For CO+O₂+H₂O, 11.4, 10.8, 14.9, and 14.3 mg of Rh/Fe(OH)_x, at reactant flow rates of 45, 30, 60, and 80 mL min⁻¹, were detected at 27, 40, 60, and 80 °C, respectively.

facilely react with CO to produce CO₂ at a rate that is 5 times higher than was previously obtained, as shown in Fig. 2. Furthermore, as shown in the Arrhenius equation profile of Fig. 7, the Ea value is significantly decreased from 22 to 9 kJ mol⁻¹ with the presence of H₂O, implying that the reaction pathway and/or rate-determining step were probably changed from CO+O to CO+OH.

Subsequently, the dominant reaction route of CO with OH species to CO₂ was verified using the time-resolved DRIFTS spectra. As shown in Fig. 8(a), O₂ and H₂O were firstly coadsorbed onto the reduced Rh/Fe(OH)_x to fabricate OH species. With purging by He for 1 h, the catalyst surface rich in OH groups was adopted as the background. After CO was injected, strong CO₂ peaks appeared with the consumption of OH species at 3600–3000 and 1630 cm⁻¹, which indicated the direct reac-

Fig. 8. Time-resolved CO-titration IR experiments at 80 °C after introducing 1 vol% CO (30 mL min⁻¹, He balanced) over the Rh/Fe(OH)_x (a) and Rh/Al₂O₃ (b) catalysts, which were pretreated by the coadsorption of O₂ + H₂O.

tion between CO and OH species to form CO₂. Meanwhile, there was an upshift of the baseline in the IR absorbance bands at high frequencies (3600–4000 cm⁻¹), which can be attributed to the formation of magnetite-like Fe₃O₄ [46,54]. This indicates the recovery of oxygen vacancies on the Fe(OH)_x support that were previously occupied by the formed OH species.

Therefore, the improved stability during the wet oxidation could be rationalized by the renewable support structure even under drastic oxidative conditions owing to the reaction between CO and OH species. As confirmed by the XRD results in Fig. 9, only diffraction peaks corresponding to Fe₃O₄ are observed over both the reduced and reacted catalysts. When we conducted similar DRIFTS experiment over the unreduced Al₂O₃ supported Rh catalyst (Fig. 8(b)), a considerably small amount of CO₂ was produced, and no variation of the OH species was observed. This is in accordance with the negligible effect of H₂O on the CO oxidation activity. Thus, the Fe(OH)_x support facilitates the activation of O₂ and H₂O to form OH species, which oxidize the adsorbed CO with a considerably small barrier, leading to the high activity and stability of the catalyst toward the wet oxidation of CO.

Notably, all PGM-based catalysts suffer from similar O₂ activation complication at ambient temperature. Since the excellent activity of the Rh/Fe(OH)_x catalyst is attributed to the facile O₂ activation in the form of OH groups on Fe(OH)_x in the presence of H₂O, it is probable that this promotional role would be also effective for other PGM catalysts. Accordingly, we investigated a series of Pt/Fe(OH)_x and Ir/Fe(OH)_x catalysts with metal dispersions forming subnanometer clusters to lower the CO adsorption strength [55,56]. It can be found in Fig. 10, that for the CO oxidation without H₂O, the CO conversions were only 20% and 5% over Ir/Fe(OH)_x and Pt/Fe(OH)_x, respectively, while almost 100% was achieved at ambient temperature via wet oxidation. These results unequivocally indicate that the reaction system of wet oxidation can be extended on a series of Fe(OH)_x-supported PGM catalysts, which facilitates the reaction between CO and the reactive OH species that originate from the

Fig. 9. XRD patterns of the reduced (1) and used (2) Rh/Fe(OH)_x samples.

Fig. 10. CO conversion with reaction temperatures, over Fe(OH)_x-supported Ir- and Pt-based catalysts during the wet oxidation process. Reaction conditions: 1 vol%CO + 1 vol%O₂, 0.6 vol% H₂O, and balanced He. WHSV= 18,000 mL g_{cat}⁻¹ h⁻¹.

adsorbed H₂O and O species, thus presenting a practical method for the abatement of CO under ambient temperature and humidity conditions.

4. Conclusions

In summary, a subnanometer Rh/Fe(OH)_x catalyst was reported as a typical example of using PGM for practical CO elimination under humid conditions. Complete CO conversion was achieved at ambient conditions and good durability with the outlet CO concentration of around 4 ppm, which shows the potential for practical application. The Fe(OH)_x support facilitates the activation of O₂ and its reaction of H₂O to form OH groups. The promotional effect of H₂O was further rationalized with kinetic studies and spectroscopic characterizations, which indicated the direct reaction between the OH species and adsorbed CO with a much lower activation energy than those of CO and O. More importantly, it is demonstrated that during the wet oxidation, the promotional role of OH groups is versatile over a series of Fe(OH)_x-supported PGM catalysts for the practical CO removal under humid conditions. Therefore, this work may serve as a quotable reference for the efficient removal of CO under ambient conditions using a relatively simple catalyst system based on PGMs.

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Graphical Abstract

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Versatile application of wet-oxidation for ambient CO abatement over $\text{Fe}(\text{OH})_x$ supported subnanometer platinum group metal catalysts

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Versatile CO abatement under ambient conditions is achieved by wet-oxidation over $\text{Fe}(\text{OH})_x$ supported subnanometer Pt group metal catalysts owing to the facile formation and reaction of hydroxyl groups.

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氢氧化铁负载亚纳米铂族金属催化剂室温湿氧化消除CO

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摘要: 室温条件下高效消除CO具有重要的意义, 但目前仍具有极大的挑战. 考虑到实际应用环境中存在的水汽, 实现具有应用价值的CO消除过程的关键是设计耐湿性好, 且能够在室温甚至更低温度下具有较高CO氧化活性的催化剂. 以Hopcalite (Cu-Mn-O_x)和Co₃O₄为代表的氧化物和负载型Au基催化剂具有优异的低温CO氧化活性, 但存在耐湿性差、催化性能重复性不好等缺点, 因而限制了其实际应用. 铂族金属催化剂凭借优异的稳定性和耐湿性成为目前最广泛应用的尾气净化催化剂. 但是由于铂金属位点强吸附CO的毒化作用, CO氧化工作温度多在200 °C以上, 从而限制了其在室内空气净化、燃料电池工业氢源净化以及汽车发动机冷启动阶段尾气净化等过程中的实际应用. 研究人员尝试调节金属粒子尺寸、金属-载体界面、双金属结构及助剂效应等以促进O₂的活化或者削弱CO的吸附, 尽管取得了一定的进展, 但仍缺少一种具有普适性和实际CO消除应用前景的铂族金属基催化体系. 本文利用新型Fe(OH)_x负载亚纳米Rh催化剂作为室温条件下CO湿氧化的典型例子, 研究H₂O对CO氧化反应的影响并探索其反应机制, 旨在为发展实际可用的CO氧化消除催化体系提供参考.

活性测试结果表明, H₂O的存在可以大幅提高Fe(OH)_x负载亚纳米Rh催化剂的CO氧化速率, 并在室温条件下实现CO的长效稳定消除; 而相似共沉淀法制备的Rh/Al₂O₃催化剂上H₂O并没有促进CO氧化. 原位红外表征发现, Fe(OH)_x在湿氧化CO过程中的重要作用在于为O₂和H₂O的吸附提供位点, 促进二者反应生成羟基物种, 并与亚纳米Rh团簇上吸附的CO反应生成CO₂. 此外, H₂O的存在使得CO氧化的表观活化能由22降至9 kJ mol⁻¹, 说明反应路径或决速步骤由CO+O转变为反应能垒更低的CO+OH, 从而大幅提高了CO氧化反应速率和反应活性. 随后, 时间分辨CO滴定红外实验证明, Rh/Fe(OH)_x催化剂表面OH可以与CO反应生成CO₂, 而Al₂O₃负载的纳米Rh催化剂则不能, 从而进一步揭示了Fe(OH)_x载体在高效湿氧化消除CO过程中的重要作用. 最后, 通过拓展实验证明该反应机理可以适用于Fe(OH)_x负载的其它铂族金属催化剂, 提供了一种具有普适性和实际CO消除应用前景的铂族金属基催化体系.

关键词: 铂族金属; 一氧化碳; 氧化; 室温条件; Fe(OH)_x; 亚纳米团簇

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