[Article]

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光还原催化剂 Pt/TiO₂ 富氢条件下 CO 优先氧化反应

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摘要: 用光还原法来提高富氢条件下 CO 优先氧化 (PROX) 催化活性和 CO₂ 选择性, 分别对有无氢气时 CO 氧化反应参数进行了详尽研究. X 射线光电子能谱 (XPS) 表征结果显示, 在光还原催化剂表面产生了部分氧空穴, 可为化学吸附 H 提供活性中心. 针对光还原 Pt/TiO₂ 催化剂上 CO 优先氧化反应提出了一种可能的双功能反应机理.

关键词: CO 优先氧化; Pt 催化剂; 光还原; 浸渍

中图分类号: O643

Preferential Oxidation of CO over Photoreduced Pt/TiO₂ Catalysts in H₂-Rich Stream

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Abstract: The optimum reaction parameters for CO oxidation in the presence and absence of H₂ have been investigated by photoreduction method to enhance the catalytic activity and selectivity of CO₂ for CO preferential oxidation (PROX) in H₂-rich stream in detail. X-ray photoelectron spectroscopy (XPS) results showed that part oxygen vacancies produced on the surface of photoreduced catalysts, which maybe the activity site for the chemisorbed H. Therefore, a possible bi-function reaction mechanism for CO preferential oxidation over the photoreduced Pt/TiO₂ catalyst has been proposed.

Key Words: CO preferential oxidation; Pt catalyst; Photoreduction; Impregnation

1 Introduction

Currently, the CO oxidation in the absence and presence of H₂ has attracted extensive attention because of its potential application in indoor or cabin air cleanup and in the purification of hydrogen streams used in proton exchange membrane (PEM) fuel cells.^{1,2} Considerable efforts have been devoted to design the suitable catalysts for the competitive oxidation of CO in the presence of hydrogen. Supported noble metals, such as Au,^{3,4} Pt,^{5–10} Pd,^{11–13} and Rh,¹⁴ were found applicable for the PROX reaction. Platinum catalysts are by far the most extensively studied catalysts owing to their superior performance in photocatalytic and thermal CO oxidation. Nevertheless, the

most commonly used Pt/TiO₂ catalysts prepared by impregnation method are unsuitable for the reaction of CO preferential oxidation since they require high operation temperature in the range of 150–200 °C. In the meantime, significant H₂ consumption can be observed in the temperature range to work effectively. Furthermore, the impregnated Pt/TiO₂ catalyst used to be pretreated by oxidation or reduction under an appropriate temperature prior to the catalytic activity tests.^{15–18} This gives an incentive for the development of a highly active and selective catalyst for CO preferential oxidation.

By comparison, the photoreduction method exhibits many advantages, such as simple operation and environment-friendly

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etc. In this study, we mainly focus on the preparation of Pt/TiO₂ catalysts by a photoreduction method. The optimum reaction parameters for CO oxidation in the presence and absence of H₂ have been investigated in detail. Based on the data of catalytic activity tests and the characterization of catalysts, a possible reaction mechanism for the PROX reaction over the photoreduced Pt/TiO₂ catalyst has been proposed.

2 Experimental

2.1 Catalyst preparation

Degussa P25 TiO₂ powder (Degussa, 70%–30% anatase) was used as a support. Before deposition, raw TiO₂ was pre-treated at 773 K for 4 h in air to stabilize its surface area and the anatase crystal form. Platinum was directly photodeposited on TiO₂ in an aqueous solution of chloroplatinic acid (1 mmol·L⁻¹) and methanol (0.1 mol·L⁻¹) under UV illumination (250 W medium-pressure mercury lamp). The samples were dried in air at 120 °C for 12 h and had no thermal treatment anymore. The theoretical mass loading amount was 1.5% (w). In order to compare with the photoreduced Pt/TiO₂ catalysts, the impregnated catalyst was reduced *in situ* at 300 °C (heating rate: 10 °C·min⁻¹) for 3 h with a 50% (volume fraction) H₂/N₂ mixture (flow rate: 60 mL·min⁻¹). The feed gas consisted of 2.5% CO and 20% O₂ in N₂ balance. In the process of PROX, a gas mixture containing 50% H₂, 1% CO, and 2% O₂ in N₂ was fed at the flow rate of 30 mL·min⁻¹. The gas phase effluents were analyzed on-line chromatographs equipped with thermal conductivity detector (TCD). At the end of the catalytic tests, the catalyst was cooled under an N₂ stream and stored for characterizations. The catalytic activities were defined in terms of conversion of CO (η), conversion of O₂, and selectivity to CO₂ (S), which were denoted as η_{CO} , η_{O_2} and S_{CO_2} , respectively, and were calculated according to the following equations:

$$h\nu=1253.6 \text{ eV}.$$

2.3 Activity measurement

Catalytic test was carried out at atmospheric pressure in a fixed bed continuous flow quartz reactor (inside diameter is 8mm), consisting of a flow controller unit, a reactor unit, and an analysis unit. A schematic diagram of the experimental system is shown in Fig.1. Typically, the temperature increased from 80 to 300 °C at a 5 °C increment, and a sample was taken for analysis after stabilizing for 30 min at each investigated temperature. Then 0.1 g catalyst diluted with equal amount of quartz was used in each run. Prior to the experiment, the impregnated catalyst was reduced *in situ* at 300 °C (heating rate: 10 °C·min⁻¹) for 3 h with a 50% (volume fraction) H₂/N₂ mixture (flow rate: 60 mL·min⁻¹). The feed gas consisted of 2.5% CO and 20% O₂ in N₂ balance. In the process of PROX, a gas mixture containing 50% H₂, 1% CO, and 2% O₂ in N₂ was fed at the flow rate of 30 mL·min⁻¹. The gas phase effluents were analyzed on-line chromatographs equipped with thermal conductivity detector (TCD). At the end of the catalytic tests, the catalyst was cooled under an N₂ stream and stored for characterizations. The catalytic activities were defined in terms of conversion of CO (η), conversion of O₂, and selectivity to CO₂ (S), which were denoted as η_{CO} , η_{O_2} and S_{CO_2} , respectively, and were calculated according to the following equations:

$$\eta_{\text{CO}} = \{([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / [\text{CO}]_{\text{in}}\} \times 100\%$$

$$\eta_{\text{O}_2} = \{([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}) / [\text{O}_2]_{\text{in}}\} \times 100\%$$

$$S_{\text{CO}_2} = \{0.5 \times [\text{CO}_2] / ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})\} \times 100\%$$

2.2 Characterization of catalysts

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku D/MAX-RB X-ray diffractometer with a Cu K α target operated at 50 kV and 40 mA with a scanning speed of 0.5 (°)·min⁻¹ and a scanning angle (2 θ) range of 10°–90°. Chemical states of the Pt species on the catalyst surface were investigated by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 210 Electron Spectrometer (Mg K α radiation;

3 Results and discussion

3.1 XRD analysis

XRD patterns of various Pt/TiO₂ catalysts were shown in Fig.2. No obvious crystallite formation of the Pt species could be found in the XRD patterns of Pt/TiO₂ (PR12) and Pt/TiO₂

Fig.1 Diagram of apparatus for the test of catalytic activity

Fig.2 XRD patterns of various catalysts

(a) Pt/TiO₂ (PR12), (b) Pt/TiO₂ (PR24), (c) Pt/TiO₂ (PR36), (d) Pt/TiO₂ (IM)

(PR24) catalysts, which indicated that the low metal content might lead to a high dispersion of Pt and, therefore, that the Pt particles were too small to be detected by XRD analysis. However, only a broader diffraction peak of Pt appeared at 39.68° for Pt/TiO₂ (PR36) and Pt/TiO₂ (IM) catalysts, which could be attributed to Pt (111).¹⁰ Therefore, the average crystallite sizes of Pt particles could be calculated by applying the Scherrer equation on the Pt (111) diffraction peaks. The calculated average crystallite sizes of Pt particles in Pt/TiO₂ (PR36) and Pt/TiO₂ (IM) samples were 16 and 10 nm, respectively. According to previous report,¹⁰ the concentrations of chlorine ions could be decreased by photoreduction, resulted in a highly dispersion of active component. These results suggested that the distribution of Pt species on the support surface could be improved by adjusting photoreduction time and the longer time will be detrimental to the enhancement of CO oxidation activity.

3.2 XPS analysis

XPS analyses were carried out to determine the surface concentration and valence state of Pt in Pt/TiO₂ catalysts. The binding energies of Pt 4f and the derived atomic contents in the different catalysts were summarized in Fig.3 and Table 1. From Fig.3 we found that the line shape and the width of Pt(4f_{7/2}, 4f_{5/2}) over the impregnated catalyst matched well with that of the metallic Pt. By comparison, the Pt 4f features obtained from the photoreduced catalysts were quite broad, both zerovalence and cationic Pt could be found. According to previous reports,^{19,20} the Pt 4f bands at 70.9 eV could be related to metallic Pt, while those at 73.2 eV could be assigned to Pt²⁺, respectively. Therefore, the relative atomic ratios of [Pt]/[Pt²⁺] decreased with the increase of photoreduction time. These results indicated that the valence state of Pt particles on the catalysts surface could be changed by adjusting photoreduction time. In addition, the atomic content on the support surface in the impregnated catalyst was much higher than those in the photoreduced catalysts, indicating that just partial Pt species could be deposited by photoreduction.

The XPS spectra of TiO₂ were also detected in order to investigate the strong metal-support interaction (SMSI) for precious metal on reducible support. It is widely accepted that such ef-

Fig.3 XPS spectra of Pt in various catalysts

(A) Pt/TiO₂ (PR12), (B) Pt/TiO₂ (PR24), (C) Pt/TiO₂ (PR36), (D) Pt/TiO₂ (IM)

Table 1 XPS data of the catalysts Pt/TiO₂ (PR12), Pt/TiO₂ (PR24), Pt/TiO₂ (PR36), and Pt/TiO₂ (IM)

Catalyst	$E_{Pt\ 4f_{7/2}}/eV$		[Pt]/[Pt ²⁺]	[Pt ²⁺]	[Pt]	[Cl]
	Pt ²⁺	Pt				
PR12	72.8	70.5	3.12	0.053	0.017	1.5
PR24	73.0	71.0	2.20	0.048	0.022	0.7
PR36	73.2	71.5	1.70	0.044	0.026	0.4
IM	—	70.9	—	0	0.31	1.2

fects may be crucial in many aspects of heterogeneous catalysis. The binding energies of TiO₂ 2p in various Pt/TiO₂ catalysts were shown in Fig.4. From Fig.4(a) we can find that the line shape and the width of TiO₂ (2p_{3/2}, 2p_{1/2}) over the impregnated catalyst matched well with those of the Ti⁴⁺, which indicated that TiO₂ could not be reduced by H₂ pretreatment. This result also suggested that there was a weak interaction between active center Pt and reducible support TiO₂. However, the binding energies of TiO₂ in photoreduced Pt/TiO₂ catalysts moved towards higher binding energy, maybe due to the production of part of Ti³⁺. According to previous report,²¹ the stoichiometric surface exists, in principle, as an oxygen vacancy and two Ti³⁺.

3.3 Activity tests

CO oxidation in the absence of hydrogen was carried out in a temperature region of 100–260 °C with a CO/O₂ molar ratio of 0.125. For comparison, CO conversions over different catalysts *versus* reaction temperature were summarized in Fig.5. It can be found that the catalytic activities for CO oxidation are

Fig.4 XPS spectra of TiO_2 for various catalysts
(a) Pt/TiO_2 (IM), (b) Pt/TiO_2 (PR12), (c) Pt/TiO_2 (PR24), (d) Pt/TiO_2 (PR36)

Fig.5 CO conversion vs reaction temperature over various catalysts

(a) Pt/TiO_2 (IM), (b) Pt/TiO_2 (PR12), (c) Pt/TiO_2 (PR24), (d) Pt/TiO_2 (PR36)

very sensitive to preparation method. Performance of the impregnated catalyst is superior to those of photoreduced ones, which maybe due to the partial deposition of the Pt species resulted from photoreduction. Although both the nature of the active Pt phase and the elucidation of the mechanism for CO oxidation are still debated, herein, we consider that the Pt oxides are major active sites. Comparing the photoreduced catalysts, we found that their catalytic performance could be significantly promoted by adjusting the photoreduction time. An optimum photoreduction time was 24 h and the longer time will be detrimental to the enhancement of CO oxidation activity. From Table 1 it can be found that the concentration of chlorine ions can be decreased from 1.5 to 0.4 when we increased photoreduction time from 12 to 36 h. Whereas the excessive photoreduction can result in the aggregation of the Pt species as shown in XRD results above. This result is consistent with previous report.²² Therefore, the Pt/TiO_2 (PR24) catalyst exhibited the best activity for CO oxidation.

Furthermore, in order to investigate the effects of H_2 , a comparison of the catalytic activities for CO preferential oxidation in the presence of H_2 between Pt/TiO_2 (IM) and Pt/TiO_2 (PR24) was made. The maximum CO conversions, the corresponding O_2 conversions and selectivities of CO_2 were shown in Fig.6. Our results showed that the maximum CO conversion of 61.4% on Pt/TiO_2 (PR24) was achieved at 180 °C, the corre-

Fig.6 Activity comparison of the CO selective oxidation between Pt/TiO_2 (PR24) (1) and Pt/TiO_2 (IM) (2) catalysts

sponding O_2 conversion and selectivity of CO_2 were 40.0% and 43.0%, respectively. However, the maximum CO conversion of 33.7% over the Pt/TiO_2 (IM) catalyst could not be obtained until the reaction temperature increased to 240 °C. Furthermore, the higher O_2 conversion of 91.4% resulted in a lower selectivity of CO_2 of 11.2%.

It has been reported that the electron transfer occurs between oxide support and Au nanoparticles or adsorbates, and influences the CO thermocatalytic oxidation.²³⁻²⁵ So, it can be proposed that the presence of H_2 may also play a similar effect on the CO oxidation via electron transfer. These results indicate that the dissociative chemisorption H at surface oxygen vacancy sites of TiO_2 deduced by photoreduction can act as both the electron-acceptors for the photogenerated electrons and the electron-donors for the chemisorbed O_2 at TiO_2 .²⁶ We consider that a bi-function reaction mechanism maybe involved in CO preferential oxidation over the photoreduced Pt/TiO_2 catalysts, where CO adsorbs on the Pt species and H_2 adsorbs at surface oxygen vacancy sites of TiO_2 . Therefore, the bi-function reaction mechanism weakens the competitive adsorption between CO and active oxygen on the Pt species, and subsequently enhances the activity for CO preferential oxidation in the presence of H_2 .

4 Conclusions

In summary, the photoreduction is an effective method to enhance the catalytic activity and selectivity of CO_2 for the reaction of PROX in H_2 -rich stream. In photoreduction process, the dissociative chemisorption H at surface oxygen vacancy sites of TiO_2 can act as the electron-donors for the chemisorbed O_2 at TiO_2 , resulted in a bi-function reaction mechanism for CO preferential oxidation in H_2 -rich stream. In addition, a further research is in progress owing to the numerous influence factors on the photoreduction, such as the irradiate intensity, the pH value, and concentration of solution, etc.

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