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控制 CO 选择氧化反应中金催化剂热点形成的新方法

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摘要: 采用沉积-沉淀法制备了 Al_2O_3 和 $\text{MO}_x\text{-Al}_2\text{O}_3$ ($\text{M}=\text{Fe}, \text{Zn}$) 负载型金催化剂. 室温下对其 CO 氧化及富氢条件下 CO 选择氧化催化活性进行了广泛的研究. 催化剂床层温度由热电偶直接测定. 催化剂表面温度与 O_2/CO 的体积比以及 CO 和 H_2 的浓度密切相关. 在 CO 氧化反应过程中 $\text{Au}/\text{Al}_2\text{O}_3$ 催化剂的温度可高达 $170\text{ }^\circ\text{C}$, 添加 FeO_x 可使其降至 $55\text{ }^\circ\text{C}$. 利用一系列仪器(X射线衍射仪, X射线光电子能谱仪和透射电镜等)对催化剂的结构进行了表征. 结果显示 Al_2O_3 负载型金催化剂热点的形成可以通过添加合适的助剂很好地控制. 助剂的添加能够使催化剂活性中心由金属态 Au 变为 Au^{III} , 从而导致了 CO 选择氧化反应机理不同.

关键词: CO 氧化; 助剂; 金催化剂; 热点

中图分类号: O643

Novel Method of Controlling Formation of Hot-Spot over Gold Catalysts for CO Oxidation

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Abstract: Au catalysts supported on Al_2O_3 and $\text{MO}_x\text{-Al}_2\text{O}_3$ ($\text{M}=\text{Fe}$ and Zn) were prepared by the deposition-precipitation method. Their catalytic activities for CO oxidation in the absence and presence of an H_2 -rich steam at room temperature were investigated in detail. Catalyst bed temperatures were determined directly by a thermocouple. The catalyst surface temperature depended on the volume ratio of O_2/CO , and the concentrations of CO and H_2 . The temperature on the $\text{Au}/\text{Al}_2\text{O}_3$ surface can reach $170\text{ }^\circ\text{C}$ during CO oxidation, and is decreased to $55\text{ }^\circ\text{C}$ by addition of FeO_x . These results indicate that formation of hot-spots on γ -alumina-supported gold catalysts could be controlled by adding an appropriate dopant. The structure of the catalysts was characterized by techniques such as X-ray powder diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy. Addition of a dopant could transfer the active center from Au to Au^{III} , which resulted in different reaction mechanisms of preferential oxidation of CO in the presence of H_2 .

Key Words: CO oxidation; Dopant; Gold catalyst; Hot-spot

1 Introduction

Au supported catalysts have been applied widely on CO oxidation in the absence and presence of H_2 owing to their attractive catalytic properties.^{1–8} Although factors that affect the performance of these catalysts, such as the Au particle size, the support, and the preparation method, have been studied extensively, studies focused on investigating formation of hot-spot

in the process of CO oxidation reaction are relative scarce.⁹ On one hand, a hot region can have a deleterious impact on the reactor performance and may deactivate the catalyst. Moreover, it may lead to severe safety problems by either initiating highly exothermic reactions, or by decreasing the material strength of the reactor wall. Base on the fact that CO and H_2 oxidations are highly exothermic reactions and the hydrogen oxidation being

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avored by higher temperatures, an effectively control of temperature is an essential measure to ensure high CO₂ selectivity. In general, the appropriate temperature can be obtained by changing the structure of reactors.^{10–14} Several design configurations have been proposed to carry out this process. Although multistaged reactors are able to handle this highly exothermic reaction system with acceptable selectivity, they have the disadvantage of requiring complex hardware to control temperatures, using staged air injections along the catalyst bed. In this paper, we mainly focus on the preparation of supported Au catalysts modified by the deposition-precipitation method. We can find that a FeO_x modified Au/Al₂O₃ catalyst is highly efficient catalyst for CO oxidation in the presence and absence of H₂. The temperature increase of catalyst bed can be effectively inhibited by addition of appropriate dopant and optimizing catalyst structure, which results in different product distribution.

2 Experimental

2.1 Catalyst preparation

The Al₂O₃-MO_x (M=Fe and Zn) composite supports were prepared by the incipient-wetness impregnation method. First, the MO_x precursor of M(NO₃)₃ (≥99.0%) were dissolved in 20 mL distilled water and mixed with calculated amount of γ-Al₂O₃ powder (129 m²·g⁻¹, 30–45 mesh). The slurry thus prepared was taken into dryness by continuous stirring and heating (60–70 °C). Then, the sample was dried at 120 °C overnight, and was subsequently calcined in air at 600 °C for 4 h. The gold-containing catalysts were prepared by the deposition-precipitation method. The adequate amount of HAuCl₄·3H₂O (Alfa, ≥99.99%) was dissolved in 150 mL of deionized water and the pH of the solution was adjusted to 8.0–9.0 by addition of 0.1 mol·L⁻¹ NaOH (≥85.0%). The solution was heated to 80 °C and then the support was added and kept under continuous stirring for 2 h. The samples obtained were washed several times with deionized water (until the disappearance of Cl⁻ and Na⁺ ions), then dried overnight at 120 °C. Fractions from the solids were finally calcined at 300 °C for 3 h. The theoretical loading amount of Au is 1.0% (*w*, mass fraction) and that of MO_x is 10% (*w*).

2.2 Characterizations of catalysts

Before each measurement, the samples were purged with dry air at 300 °C for 1 h. Chemical states of Au nanoparticles on the catalysts surface were investigated by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 210 Electron Spectrometer (Mg K_α radiation; *hν*=1253.6 eV). XPS data were calibrated using the binding energy of C 1s (285.0 eV) as the standard. The transmission electron microscopy (TEM) images were obtained on a transmission electron microscope (JEM1200-EX, JEOL) with an accelerating voltage of 80 kV. A drop of the solution containing Au nanoparticles was put onto a carbon-supported copper mesh, which was dried at room temperature. High-resolution transmission electron microscopy (HRTEM) images were obtained on a transmission electron mi-

croscope (JEM2010, JEOL) with an accelerating voltage of 200 kV. The specific surface area of the catalyst was measured by the Brunauer-Emmett-Teller (BET) method on a Micromeritics ASAP-2010 apparatus at liquid nitrogen temperature with N₂ as the absorbent at 77 K.

2.3 Activity measurement

Catalytic test was carried out at atmospheric pressure in a fixed bed continuous flow quartz reactor (inner diameter, i.d. 8 mm), consisting of a flow controller unit, a reactor unit, and an analysis unit. Typically, 100 mg of the catalyst was used in each run. The total flow rate of the feed gas was 60 mL·min⁻¹ (gas hourly space velocity (GHSV)=36000 h⁻¹). The feed gas consisted of 5%–20% (*φ*, volume fraction) of CO and 20% (*φ*) O₂ in N₂ balance. In the process of PROX, a gas mixture containing 55%–25% (*φ*) H₂, 2%–5% (*φ*) CO, and 1%–2% (*φ*) O₂ in N₂ was fed at the flow rate of 30 mL·min⁻¹. Argon was used as the carrier gas and nitrogen was used as the internal standard for gas analysis. 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*_{CO}), conversion of O₂ (*η*_{O₂}), and selectivity to CO₂ (*S*), and were calculated according to the corresponding equations:

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

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

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

where [CO]_{in} or [O₂]_{in} is intake concentration, [CO]_{out} or [O₂]_{out} is outtake concentration, [CO₂] is production CO₂ concentration.

3 Results and discussion

3.1 Activity tests

Traditionally, the temperature of catalyst bed measured by thermocouple, as shown in Fig.1(a), could be considered as the reaction temperature. Obviously, it is inaccurate because of external and internal heat transfer hysteresis. We modified the temperature measure system as shown in Fig.1(b), here, thin layer catalyst particles were sandwiched between two inactive quartz sands in tube reactor, the reaction tube was embedded in an adiabatic reactor. In this case, catalyst bed temperature can

Fig.1 Schematic representation of different reactors

be obtained directly by thermocouple and its increase completely derives from the exothermic reactions. Although it is difficult to determine the catalyst bed absolutely because it is much dependent on the size, we think it is possible to obtain a relative tendency of the bed temperature behavior qualitatively.

The catalytic activities for CO oxidation in the presence and absence of H_2 on the original and MO_x ($M=Fe, Zn$) doped Au/Al_2O_3 catalysts were investigated at ambient temperature. All catalysts exhibited attractive performances for CO oxidation in the absence of H_2 . CO could be eliminated even when its concentration increased to 20%. However, no measurable activity could be found over Au/Al_2O_3 when H_2 was introduced in reaction stream. The stabilities of both catalysts dopanted by MO_x were tested in the reaction of CO selective oxidation in the presence of H_2 and the results were shown in Fig.2. CO could be converted completely and the CO_2 selectivities over $Au/FeO_x-Al_2O_3$ and $Au/ZnO-Al_2O_3$ were 95% and 92%, respectively, even after 100 h. In addition, effects of the volume ratio of O_2/CO on CO conversion and CO_2 selectivity for PROX over $Au/FeO_x-Al_2O_3$ were also measured as shown in Fig.3. It can be found that CO conversion can be stabilized at 100% when the volume ratio of O_2/CO increased from 0.5 to 1.0, however, the CO_2 selectivity decreased from 95% to 50%.

Based on their attractive catalytic performances, the surface temperatures over various Au catalysts were studied in CO oxidation reaction as shown in Fig.4. All catalyst surface tempera-

tures were enhanced significantly by increasing CO concentration in the reaction stream, owing to reaction exotherm increase. The maximum temperature obtained from Au/Al_2O_3 was 160 °C when CO concentration was raised to 20%, whereas the corresponding temperature on the FeO_x doped catalyst was just 55 °C. It is interesting to note that the Au/Al_2O_3 catalyst surface temperature could be decreased dramatically by FeO_x addition, especially in higher CO concentration. However, their surface temperatures were enhanced obviously by ZnO addition, a maximum temperature of 170 °C could be obtained. The surface temperatures over different Au catalysts in CO selective oxidation in the presence of H_2 for PROX reaction were also shown in Fig.5. Marwaha *et al.*¹⁵ reported that heat generation and heat removal significantly determined the change of product distribution depending on the contact. In order to eliminate effect of contact time, the catalyst surface temperatures were studied in the same space velocity. No detectable temperature changes could be found on the Au/Al_2O_3 catalyst surface because of its low catalytic activity for PROX reaction. However, the surface temperatures on both MO_x modified catalysts could be increased in a certain extent by raising H_2 concentration in the reaction stream. For the $Au/FeO_x-Al_2O_3$ catalyst, a maximum temperature of 55 °C was obtained when CO and H_2 concentrations were 2.5% and 50%, respectively. However, the surface temperature of the $Au/ZnO-Al_2O_3$ catalyst could achieve 105 °C, and the high temperature resulted in

Fig.2 Stability test of the $Au/MO_x-Al_2O_3$ ($M=Fe, Zn$) catalysts for CO selective oxidation in the presence of H_2

Fig.3 Effects of the volume ratio of O_2/CO on CO conversion and CO_2 selectivity for PROX over $Au/FeO_x-Al_2O_3$

Fig.4 Catalyst surface temperatures in CO oxidation reaction

Fig.5 Catalyst surface temperatures in PROX reaction

decrease of the corresponding CO₂ selectivity. The surface temperature transformation of FeO_x modified catalyst was less than 5 °C when H₂ concentrations were increased from 40% to 55%, while CO concentrations were decreased from 4% to 2.5%. These results proved further that the Au/FeO_x-Al₂O₃ catalyst is an appropriate candidate for CO oxidation in the absence and presence of H₂. Furthermore, the surface temperatures were much dependent on the volume ratio of O₂/CO, which might due to that higher ratios were beneficial to the oxidation of hydrogen as shown in Fig.3.

Five main reactions involved in a PROX reactor include:

In order to reduce the complexity, only the reactions with significant rates were considered (CO and H₂ oxidation). The catalyst surface temperature in the adiabatic reactor can be calculated according to the equations¹⁶ below:

$$T_s - T_g = \frac{k_A(-\Delta H_r)}{a_s a_m}$$

$$a_s = \frac{j_H G C_p}{P_r^{2/3}}$$

$$j_H = \frac{1.10}{R_e^{0.41} - 0.15}$$

where T_s is catalyst surface temperature, T_g is reaction mixed-gas temperature, a_s is coefficient of heat transfer, a_m is effective external surface area of catalyst bed per quality unit, and ΔH_r is exotherm from CO and H₂ oxidation reactions. C_p is heat capacity of the reaction mixture under constant pressure, and j_H is heat transfer factor, while k_A and G are reaction rate and mass rate of the reaction mixed-gas. In this case, we consider that the influence of a_s and ΔH_r on Au catalysts surface temperature can be negligible. It is, however, T_s rather than T_g controls the reaction rate k_A and also the selectivity of a heterogeneous catalytic process through the Arrhenius equation ($K = A \exp(-E_a/RT_s)$).¹⁷ The exponential in Arrhenius' expression for a rate constant has, in fact, not one but two variables, E_a and T_s , which could vary with the imposed experimental conditions and the resulting reaction rates. The traditional interpretation is that the activation energy E_a can be calculated from T_s and the corresponding reaction rates or rate constants. Thus, k_A and a_m are

the factors that can affect the catalyst surface temperature.

3.2 Characterization of catalyst

In order to investigate the relationship between various catalyst structures and their surface temperature, a series of characterizations were carried out on various Au catalysts. XPS spectra of Au 4f over the original and MO_x doped Au/Al₂O₃ catalysts are shown in Fig.6. The line shape and width of Au 4f over the original Au/Al₂O₃ catalyst matched well with those of the metallic Au, indicating that zerovalence gold was the active center for CO oxidation at low-temperature. By comparison, the Au 4f features obtained from MO_x modified Au/Al₂O₃ were quite broad, both zerovalence and cationic gold could be found, which were consistent with the Au/Fe₂O₃ catalyst reported previously.¹⁸ In addition, we can find that the Au^{III}/Au⁰ molar ratio was 53% over Au/ZnO-Al₂O₃, while that increased to 74% over Au/FeO_x-Al₂O₃ catalyst. The result indicated that the valent state of gold particles on the catalyst surface could be changed by MO_x addition. It is already well proven that both Au^{III} and Au⁰ species are active for CO oxidation.¹⁹ Once the catalyst is exposed to a CO/O₂ mixture, the Au^{III}/Au⁰ molar ratio decreases and after a sufficiently long exposure only metallic gold is left. This result proves that the lattice oxygen of cationic gold does participate in the reaction of CO oxidation. However, it is should be noted that the decline in activity was not observed when high CO flow rates were employed even for 100 h. The XPS result from Au/FeO_x-Al₂O₃ catalyst showed that no Au^{III}/Au⁰ ratio decline could be found. We consider that cationic gold species does not participate in CO oxidation at low temperature, which maybe play an important role at higher temperature. In other words, the decline in activity caused by the decrease of Au^{III}/Au⁰ molar ratios can be inhibited by controlling the hot spot temperature.

TEM and HRTEM images from different supported Au catalysts are shown in Fig.7 and Fig.8. The Au nanoparticles on all catalysts had a uniform size around 5 nm and were well dispersed and embedded in mesostructured support matrix. The fringes in Fig.8(a) gave a d -spacing of 0.24 nm, corresponding to the (111) atomic planes of gold lattice. This result shows that the catalysts surface temperature difference can not be attributed to the active component particle size, which is distinguished from NiO/Al₂O₃ catalyst reported previously.²⁰ Both polycrystal and single crystal of gold particles coexisted over Au/FeO_x-Al₂O₃, the degree of crystallinity was much lower

Fig.6 XPS spectra of Au 4f on various catalysts

(a) Au/Al₂O₃, (b) Au/ZnO-Al₂O₃, (c) Au/FeO_x-Al₂O₃

Fig.7 TEM images of different catalysts

(a) Au/Al₂O₃; (b) Au/FeO_x-Al₂O₃; (c) Au/ZnO-Al₂O₃

Fig.8 HRTEM images of various catalysts

(a) Au/Al₂O₃; (b) Au/FeO_x-Al₂O₃; Inset in Fig.8 shows the corresponding selected area electron diffraction pattern.

than that on the Au/Al₂O₃ catalyst. Furthermore, the Au lattice on Au/FeO_x-Al₂O₃ preferred to become strongly distorted so as to adopt the lattice dimensions of the mixed-oxide support, which is similar to Au nanoparticles supported on TiO₂.²¹ These results indicated that there was a strong interaction between Au and FeO_x. Density functional theory (DFT) calculations have shown that lattice strain may enhance surface reactivity.²² It has been suggested to explain the unusually high low-temperature CO oxidation activity of small Au particles. In addition, the pore structure parameters of all catalysts from the N₂ adsorption-desorption isotherms are given in Table 1. The surface area, pore volume, and average pore size of the Au/Al₂O₃ catalyst are 185.0 m² · g⁻¹, 0.43 cm³ · g⁻¹, and 8.8 nm, respectively. The surface area and average pore size were decreased slightly by ZnO addition. However, it is interesting to note that the surface area of Au/FeO_x-Al₂O₃ is smaller than that of the Au/Al₂O₃ catalyst, whereas its average pore size is obviously larger, which maybe due to that FeO_x inhibited part small pores of Al₂O₃.

Based on the foregoing observations and discussions, we can summarize schematically the adsorption of CO, O₂, and/or H₂ on both catalysts. The difference of the catalyst surface temperatures might mainly due to various active centers, which can result in different reaction mechanisms. With respect to the Au/Al₂O₃ catalyst, support Al₂O₃ usually can be regarded as chemical inert for CO oxidation. The role of the support material is limited to the stabilization of very small gold particles. Thus, oxygen adsorption and dissociation must be possible on the metallic Au nanoparticles. In this case, the activity seems to de-

Table 1 Textural properties of different catalysts obtained by N₂ adsorption

Catalyst	Surface area (m ² · g ⁻¹)	Pore volume (cm ³ · g ⁻¹)	Average pore size nm
Au/Al ₂ O ₃	185.0	0.43	8.8
Au/FeO _x -Al ₂ O ₃	167.4	0.44	10.0
Au/ZnO-Al ₂ O ₃	157.8	0.34	7.2

pend very critically on the diameter of the gold particles and only extremely small particles cause highly active samples. No PROX reaction occurs because the active sites are fully covered with H₂ or CO strongly adsorbed on the Au/Al₂O₃ catalyst due to blocked access of O₂ to the reaction sites. This strongly indicates that a dissociative adsorption of O₂ and the following surface reaction with preadsorbed CO are essential for PROX reaction, similar to Langmuir-Hinshelwood mechanism.²³ While for the Au/FeO_x-Al₂O₃ catalyst, on one hand, CO oxidation reaction can occur at the interface between Au and FeO_x, just as the Au/Fe₂O₃ catalyst.²⁴ Moreover, the addition of FeO_x can enhance the oxygen vacancy, which is in favor of the adsorption of CO and active oxygen species. Therefore, the Au/FeO_x-Al₂O₃ catalyst is very effective for the inhibition of the hot spot formation in CO oxidation reaction, mainly due to the low oxygen affinity of Au,²⁵ which results from FeO_x modification. Furthermore, the low temperature of hot spot may be also related to the enhancement of effective external surface area of catalyst bed per quality unit. Herein, we think that there maybe a so-called bi-functional mechanism existed over the Au/FeO_x-Al₂O₃ catalyst in PROX reaction, just as the Pt-Fe/mordenite catalysts reported previously.²⁶ Where Au sites are available for the adsorption of CO as well as H₂, and the FeO_x site acts as an O₂ dissociative-adsorption site. CO adsorbed on a Au site and O₂ adsorbed on an Fe site react immediately at low temperature once both reactants sit on such neighboring site. The mechanism could not only well explain the excellent catalytic performance of the Au/FeO_x-Al₂O₃ catalyst, but also might be responsible for the surface temperature difference between FeO_x and ZnO modified catalysts.

4 Conclusions

In summary, the Au/MO_x-Al₂O₃ (M=Zn, Fe) catalysts with

high CO oxidation catalytic performances in the absence and presence of H₂ have been synthesized successfully. The temperature increase of catalyst bed can be effectively inhibited by addition of appropriate dopant and optimizing catalyst structure, which results in different product distribution. Reaction path of CO oxidation over alumina supported gold catalyst can be well controlled by the addition of FeO_x through regulating the oxidation state of Au species. The result opens an alternative line in the investigations on better and more selective catalyst materials.

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