Gold Catalyst in PROX: The Role of Dopant and Reaction Exothermicity

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Keywords: Gold Catalyst, CO Oxidation, Exothermicity.

Abstract. Reaction exothermicity over γ-alumina supported gold catalysts could be well controlled by adding appropriate dopant. The addition of adopant FeOx and CeO_2 could transfer active species Au^0 to Au^{III} resulted in different reaction mechanism of CO oxidation in the absence and presence of H_2.

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]. 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 reaction exothermicity in the process of CO oxidation reaction are relative scarce. On the 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 favored by higher temperature, an effectively control of temperature is an essential measure to ensure high CO_2 selectivity. In general, the appropriate temperature can be obtained by changing the structure of reactors [2]. Several design configurations have been proposed to carry out this process. In spite of 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, a novel method, i.e. adding an adopant on the catalyst surface was discovered and reaction exothermicity could be controlled effectively.

Traditionally, the tube furnace temperature measured by thermocouple 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, here, thin layer catalyst particle were sandwiched between two inactive quartz sand in tube reactor, the reaction tube was embedded in adiabatic reactor. In this case, the catalyst bed temperature can be obtained by thermocouple and its increase is derived from the exothermic reactions. Although it is difficult to determine the reaction exothermicity absolutely because it is much dependent on the size, we think it is possible to obtain the relative tendency of the reaction exothermicity behavior qualitatively.

The catalytic activities for CO oxidation in the presence and absence of H_2 on the original and MOx (M=Fe and Ce) doped Au/Al_2O_3 catalysts were investigated at ambient temperature. Based on their attractive catalytic performances for CO oxidation in the absence of H_2, the surface temperatures over various Au catalysts were studied as shown in Fig.1(left). All catalysts surface temperatures 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^oC when CO concentration was raised to 20%, whereas the corresponding temperature on the Fe_2O_3 and CeO_2 doped catalyst was just 55^oC and $100\ ^oC$, respectively. It is interesting to note that the Au/Al_2O_3 catalyst surface temperature could be decreased dramatically by FeOx addition, especially in higher CO concentration. The surface temperatures over different Au catalysts in PROX reaction are also shown in Fig.1(right). Marwaha et.al [3] reported that heat generation and heat removal significantly determine the change of product distribution depending on the contact. In

order to except 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 MOx modified catalysts could be increased in a certain extent by raising H_2 concentration in the reaction stream. For the Au/Al_2O_3-FeOx catalyst, a maximum temperature of 55°C was obtained when CO and H_2 concentration were 2.5% and 50%, respectively. However, the surface temperature of the Au/Al_2O_3-CeO_2 catalyst could achieve 82°C, and the high temperature resulted in decrease of the corresponding CO_2 selectivity. The surface temperature transformation of FeOx modified catalyst in the region of 5°C when H_2 concentrations were increased from 40% to 55%, while CO concentrations were decreased from 4% to 2%. These results proved further that the Au/Al_2O_3-FeOx catalyst is an appropriate candidate for CO oxidation in the absence and presence of H_2.
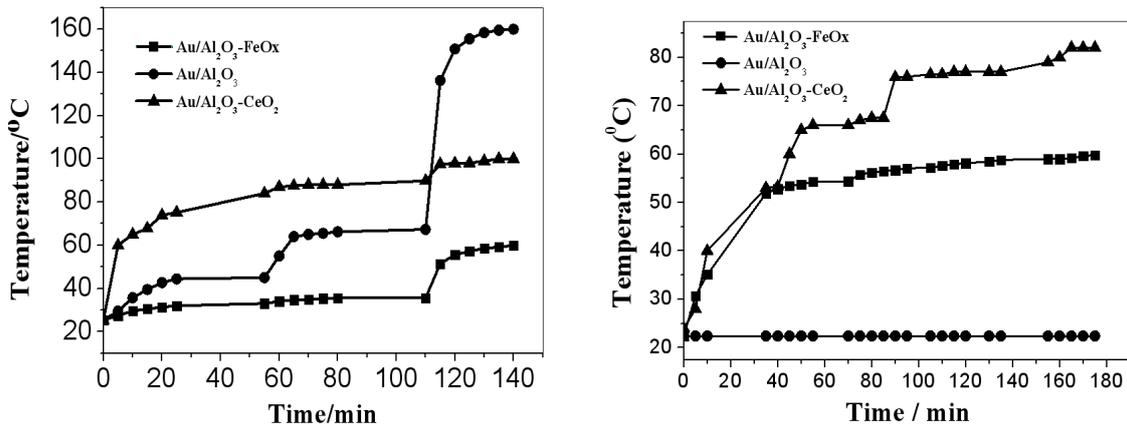
Fig.1 The catalysts surface temperatures for CO oxidation in the absence and presence of H_2

In order to reduce the complexity, only the reactions with significantly rates are considered (CO and H_2 oxidation). The catalyst surface temperature in the adiabatic reactor can be calculated according to the equations [4] below:

$$T_S - T_g = \frac{\kappa_A(-\Delta H_r)}{\alpha_s \alpha_m} \qquad Eq.1$$

$$\alpha_s = \frac{j_H G C_P}{(Pr)^{2/3}} \qquad Eq.2$$

$$j_H = \frac{1.10}{(Re)^{0.41} - 0.15} \qquad Eq.3$$

Where Tg is reaction mixed-gas temperature, α_s is coefficient of heat transfer, α_m is effective external surface area of catalyst bed per quality unit, and ΔHr is exotherm from CO and H_2 oxidation reactions. Cp 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 α_s and ΔHr on Au catalysts surface temperature can be negligeable. It is, however, Ts rather than Tg that controls the reaction rate k_A and also the selectivity of a heterogeneous catalytic process through the Arrhenius equation (K=Aexp(-Ea/RTs)) [5]. The exponential in Arrhenius' expression for a rate constant has, in fact, not one but two variables, Ea and Ts, which could vary with the imposed experimental conditions and the resulting reaction rates. The traditional interpretation is that the activation energy Ea can be calculated from Ts and the corresponding reaction rates or rate constants. Thus, k_A and α_m are the factors that can affect the catalyst surface temperature.

Tab.1 XPS data of different catalysts

Catalyst	Center(Au)	Au^{III}/Au	Au(AT)%
Au/Al_2O_3	83.62	0	0.052
$Au/Al_2O_3-CeO_2$	83.76	1.8	0.054
$Au/Al_2O_3-Fe_2O_3$	83.84	3.0	0.056

In order to investigate the relationship between various catalysts structure and their surface temperature, a series of characterizations were carried out on various Au catalysts. XPS spectra of Au4f over the original and FeOx doped Au/Al_2O_3 catalysts are shown in Table 1. The line shape and width of Au4f over the original Au/Al_2O_3 catalysts matched well with those of the metallic Au, indicating zerovalence gold was the active center for CO oxidation at low-temperature. By comparison, the Au4f feature obtained from Au/Al_2O_3-FeOx was quite broad, both zerovalence and cationic gold could be found, which was consistent with the Au/Fe_2O_3 catalyst reported previously [6]. In addition, we can find that the surface atomic concentration is similar,but the Au^{III}/Au^0 molar ratio was 1.8 over $Au/ZnO-Al_2O_3$, while that increased to 3.0 over $Au/FeOx-Al_2O_3$ catalyst. The result indicated that the valent state of gold particles on the catalyst surface could be changed by adopant addition. It is already well proven that both Au^{III} and Au^0 species are active for CO oxidation [7].Once the catalyst is exposed to a CO/O_2 mixture, the Au^{III}/Au^0 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. The XPS result from $Au/FeO_X-Al_2O_3$ catalyst showed that no Au^{III}/Au^0 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 Au^{III}/Au^0 ratios decrease can be inhibitted by controlling the hot spot temperature.
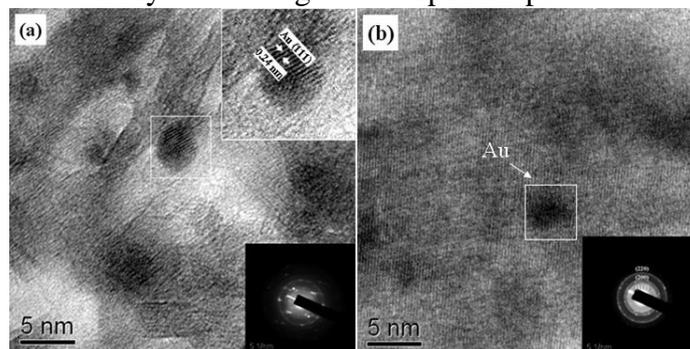
Fig.2 HRTEM images of (a) Au/Al_2O_3; (b) $Au/Fe_2O_3-Al_2O_3$

HRTEM images from different supported Au catalysts are shown in Fig.2. 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.2(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/Al_2O_3 catalyst reported previous [8]. Both polycrystal and single crystal of gold particles coexisted over $Au/FeOx-Al_2O_3$, the degree of crystallinity is much lower than that on the Au/Al_2O_3 catalyst. Furthmore, the Au lattice on $Au/FeO_x-Al_2O_3$ prefers to become strongly distorted so as to adopt the lattice dimensions of the mixed- oxide support, which is similar to Au nanoparticles supported on TiO_2 [9]. These results indicated that there was a strong interaction between Au and FeO_x. DFT calculations have shown that lattice strain may enhance surface reactivity [10]. It has been suggested to explain the unusually high low-temperature CO oxidation activity of small Au particles.

Based on the foregoing observations and discussions, we can summarize schematically the adsorption of CO, O_2 and/or H_2 on three catalysts. The difference of the catalysts surface temeratures might mainly due to various active centers, which can result in different reaction mechanisms. With respect to the Au/Al_2O_3 catalyst, support Al_2O_3 usually can be regarded as

chemical inert for CO oxidation. Thus, oxygen adsorption and dissociation must be possible on the metallic Au nanoparticles. No PROX reaction occurs because the active sites are fully covered with H_2 or CO strongly adsorbed on the Au/Al_2O_3 catalyst due to blocked access of O_2 to the reaction sites. This strongly indicates that a dissociative adsorption of O_2 and the following surface reaction with preadsorbed CO are essential for PROX reaction, similar to Langmuir-Hinshelwood mechanism. While for the Au/Al_2O_3-MO_x catalyst, on the one hand, CO oxidation reaction can occur at the interface between Au and the adopant MO_x, just as the Au/Fe_2O_3 catalyst [11]. Moreover, the addition of MO_x can enhance the oxygen vacancy, which is in favor of the adsorption of CO and active oxygen species. Therefore, the Au/Al_2O_3-MO_x catalyst are very effective for the inhibition of the hot spot formation in CO oxidation reaction, mainly due to the low oxygen affinity of Au [12], which resulted from MOx modification. Herein, we think that there maybe a so-called bifounctional mechanism exist over the Au/Al_2O_3-MO_x catalyst in PROX reaction, just as the Pt-Fe/Mordenite catalysts reported previously [13]. Where Au sites are available for the adsorption of CO as well as H_2, and the FeO_x site acts as an O_2 dissociative-adsorption site. CO adsorbed on a Au site and O_2 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/Al_2O_3-MO_x catalyst, but also might be responsible for the surface temperature difference between FeOx and CeO_2 modified catalysts.

In summary, the Au/MO_X-Al_2O_3 (M=Ce and Fe) catalysts with high CO oxidation catalytic performances in the absence and presence of H_2 have been synthesized successfully. Reaction exothermicity could be well controlled by adding adopant. The result opens an alternative line in the investigations on better and more selective catalyst materials.

Acknowledgments

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