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THE INFLUENCE OF TRANSITION METALS ON THE PERFORMANCE OF Pt Rh Pd/γ-AL_2O_3 THREE WAY CATALYSTS FOR PURIFICATION OF AUTOMOTIVE EXHAUST GAS

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ABSTRACT. The influences of transition metal oxides (Zr, Mn, Co, Cu, Mo) on the performance of Pt Rh Pd/γ-Al_2O_3 three way catalysts were studied. The characteristics of the catalysts are investigated by using XRD, TPD, TPR. Experimental results show that the addition of Zr, Mn, Co, and Cu promoters improved the activity of Pt Rh Pd/γ-Al_2O_3 catalyst remarkably for CO, CH and NO_x conversion, respectively. The effective order of the promoters is CuO > ZrO_2 > Co_3O_4 > MnO_2. The addition of CuO improved the dispersion of the noble metal on the γ-Al_2O_3 support and increased the absorption of Pt Rh Pd/γ-Al_2O_3 catalyst for CO and O_2, in addition, promoted the reduction of the noble metal.

KEY WORDS: Purification of exhaust gas, Pt Rh Pd/γ-Al_2O_3 catalyst, Transition metals

INTRODUCTION

Today, automobile prevails across the globe as the most popular and necessary mode of transportation in our daily lives. About 50 million cars are produced every year, and over 700 million cars are used worldwide. Thus, the use of catalysts for purifying exhaust gases, which contains pollutants such as carbon monoxide (CO), hydrocarbon (HC), nitrogen oxides (NO_x), is absolutely necessary and indispensable in every vehicle. Catalysts are composed of several components, the main active components are the noble metals Pt, Pd and Rh, alumina-based supports with a high surface area and a mixture of base-metal additives, mainly oxides of Ce, Zr, La, Ni, Fe, alkaline-earths, etc [1].

As we know, Pd and Pt are very effective in oxidizing CO and hydrocarbons, they are substantially less effective in reducing NO_x emissions. Pd and Pt are relatively ineffective for the dissociative chemisorption of NO [2, 3], in contrast to Rh, which is a key component responsible for NO_x reduction in purifying exhaust gases [4]. Pt Pd Rh three way catalysts (TWCs) are widely adopted for purification of automotive exhaust gas in order to eliminate the contaminations of CO, CH and NO_x [1, 5]. The following reactions occur:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$C_xH_y + (x + \frac{1}{4}y)\ O_2 = x\ CO_2 + (\frac{y}{2})\ H_2O$$

$$NO + CO \rightarrow CO_2 + \frac{1}{2}N_2$$

$$(2x + \frac{y}{2})NO + C_xH_y \rightarrow xCO_2 + (x + \frac{y}{4})N_2 + (\frac{y}{2})H_2O$$

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Burch [6] *et al.* research a series of Pt/γ-Al_2O_3 catalysts promoted by metal oxides (Ba, Ce, Co, Cs, Cu, K, La, Mg, Mo, Ti) and tested for the lean NO_x reaction using C_3H_6 as a reductant. The promoters Ce, Co, Cu, K, Mo, Ti were beneficial to the activity of Pt/γ-Al_2O_3 catalyst for NO_x conversion, and the order of the activity of catalysts are Pt-Mo/γ-Al_2O_3 >Pt-Ti/γ-Al_2O_3 > Pt-Cu/γ-Al_2O_3 ≈ Pt-K/γ-Al_2O_3 > Pt-Ce/γ-Al_2O_3. Gutierrez *et al.* [7] investigated Pt-Co based catalysts for the selective catalytic reduction of NO_x with CH_4. They found that there are interact between Co and Pt and the Pt-Co catalyst was more active than the Pt based catalyst. Konsolakis *et al.* [8] examined the effect of Ba on reduction of NO by propene over Pt catalysts supported on γ-Al_2O_3. Both catalytic activity and selectivity are strongly promoted by Ba. Gauthard *et al.* [9] investigated supported bimetallic palladium and platinum catalysts promoted by metals of group IB (Cu, Ag, and Au) and tested in the liquid-phase reduction of nitrates. The addition of Cu and Ag improved the active expect Au and the characterization results have been correlated with the metal-metal interaction and the localization of the promoter.

The previous studies of the promoters to single (or double) noble metal catalysts are concentrated in the field of reduction of NO_x and nitrates. However, no report on the promotional effect of transition metals on the catalytic performance of the trimetallic Pt Pd Rh TWCs to eliminate the contaminations of CO, CH and NO_x has been seen. The study of the role of transition metals in trimetallic Pt Pd Rh catalysts has important meanings [6-8]. In this work a number of transition metal oxides (Zr, Mn, Co, Cu, Mo) promoted Pt Rh Pd/γ-Al_2O_3 TWCs have been prepared and tested with a view to improving the catalyst activity.

EXPERIMENTAL

Preparation of catalysts

Pt Rh Pd/γ-Al_2O_3 catalyst was prepared by impregnating γ-alumina (surface area of 167 m^2/g), calcined in air at 773 K for 2 h, with Pt Rh Pd mixed solution, dried at 383 K for 2 h and calcined at 773 K for 4 h. Pt Rh Pd-TM/γ-Al_2O_3 catalysts were prepared firstly by a stepwise impregnation of γ-Al_2O_3 with a transition metal nitrate solution [10], dried and then calcined, followed by impregnation with a Pt Rh Pd solution. Other steps are the same as the preparation of the Pt Rh Pd/γ-Al_2O_3 catalyst (content of mixing noble metals was 0.06 mol %, and the Pt : Rh : Pd = 3 : 1 : 3 (mol); the loading of transition metal (Zr, Mn, Co, Mo) was all 0.78 mol% and Cu was 0.78-3.12 mol %).

Measurement of catalytic activities

The catalytic activities were tested in a continuous flow microreactor. Catalyst (100 mg) was reduced first in flowing H_2 (60 mL/min) at 673 K for 2 h, then a mixture gas was directed into the reactor (according to the stoichiometric ratio of the reaction, the component of the mixture gas was CO 3.5 vol.%, NO 1.0 vol.%, C_3H_8 1.0 vol.%, O_2 6.2 vol.%, remainder was N_2, offered by the special gas company of East China), GHSV 20000 h^{-1}, reaction temperature 473-773 K. The gas composition was analyzed before and after the reaction by an online gas chromatography with thermal conductor detector (TCD), connected with a computer integrator system and using TDX-01 and Porapak Q columns. The activity of the catalysts was expressed by the conversion of CO, CH, and NO_x, respectively.

$$x = \frac{C - C'}{C} \times 100\%$$

where x is the conversion, C the mol concentration of the reactant before the reaction, C' the mol concentration of the reactant after the reaction.

X-ray diffraction

X-ray diffraction measurements for structure determination were carried out with a Regaku model D-Max-RB diffractometer equipped with a rotating anode and Cu Kα radiation, and operating at 40 kV and 30 mA, with a scanning rate of 4^o/min.

Temperature-programmed desorption (TPD)

The samples (300 mg) were reduced by heating to 673 K for 2 h in H_2 (50 mL/min). The hydrogen flow was stopped and the system was purged with argon (40 mL/min). The samples were heated to 973 K at a rate of 8 K/min, followed by cooling to room temperature. The absorbing gas (CO or O_2) was pulsed until saturated. The samples were then heated to 973 K (8 K/min) for recording the TPD spectra.

Measurement of the dispersion

H_2 chemisorption experiments were used to measure the dispersion. Each sample was reduced at 673 K for 2 h in a flow of H_2 (50 mL/min) and cooled in pure N_2 before H_2 chemisorption measurements. The pulsing gas was H_2, the loop volume was 0.52 mL, and the chemisorption temperature was maintained at 293 K. The H_2 chemisorption capacity of sample was confirmed using a static volumetric method. Assuming Pt : H, Pd : H and Rh : H adsorption stoichiometries of 1 : 1, the number of active atoms of noble metal on per unit mass catalyst (N_a) are equal to the number of H chemisorption [11]. The dispersion is defined by:

$$D = N_a / N_T$$

where N_T is the total number of noble metals on per unit mass catalyst.

Temperature-programmed reduction (TPR)

In order to remove impurity absorbed before 973 K on catalyst surface, the samples (400 mg) were heated to 973 K in high purity nitrogen (99.99%) and kept at this temperature until the base line was straight, After cooling to room temperature, TPR experiments were performed from room temperature up to 973 K in 10% H_2/N_2 with a flow rate of 60 mL/min.

RESULTS AND DISCUSSION

Effect of transition metal on Pt Rh Pd /γ-Al_2O_3 catalyst for CO oxidation

Influences of transition metal oxides (Zr, Mn, Co, Cu, Mo) on the activity of the Pt Rh Pd /γ-Al_2O_3 catalyst for CO oxidation are shown in Figure 1. The results show that the addition of ZrO_2, MnO_2, Co_3O_4, CuO promoters improved the activity of the catalyst remarkably except Mo, the effective order of the promoters is CuO > ZrO_2 > Co_3O_4 > MnO_2. According to the literature reports, CO oxidation over CuO, MnO_2, Co_3O_4 and ZrO_2 have been studied. Co_3O_4 and CuO have higher activity for CO than the other metal oxides [12]. Teng investigated the CO oxidation in 300-600 K, the result showed that the order of activity for CO oxidation is Co_3O_4 > CuO > MnO_2 [13]. Comparing the order of activity of transition metal oxides to act as catalyst alone and to appear as promoters in Pt Rh Pd /γ-Al_2O_3catalyst, we found that the two order of activity is inconsistent. It shows that the transition metal not totally being in the form of an oxide in the Pt Rh Pd-TM/γ-Al_2O_3 catalysts, but generating certain synergistic effects as a result of the effect of transition metal oxide with noble metals which is favorable to improve the activity of the catalyst.

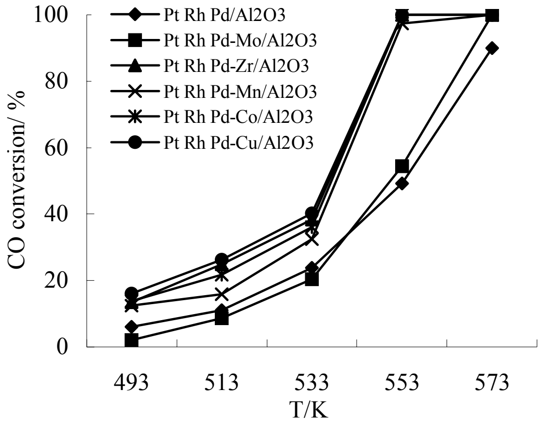

Figure 1. Effect of transitions metal oxides on the catalytic activity for CO oxidation.

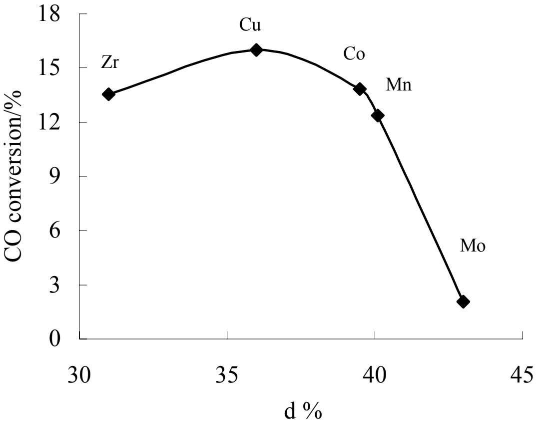

Figure 2. Correlation between d% of TM and catalytic activity.

Percentage d-character is an empirical indicator of the electronic structure of the metal [14]. As the name implies, percentage d-character refers to the contribution of the d-electrons to the spd hybrid orbitals assumed in Pauling's resonance valence band theory [15, 16]. Figure 2 (drawn with the aid of Deng's data [17]) shows the correlation of the performance of the Pt Rh Pd-TM/γ-Al_2O_3 catalysts with the percentage of the d character (d%) of TM. The best activity of the catalysts can be seen when d% increase to 36. There is a close relationship between the d% and catalytic activity. An ideal d% will result in a useful improvement in catalyst effectiveness.

Effect of Cu on Pt Rh Pd /γ-Al_2O_3 catalyst for CO, CH oxidation and NO reduction

Figure 3 shows the influence of Cu loading on activity of Pt Rh Pd /γ-Al_2O_3 catalyst for CO and CH oxidation. It can be seen that the activity of the Pt Rh Pd-Cu /γ-Al_2O_3catalyst increases with the increase of the content of copper. CO conversion of Pt Rh Pd/γ-Al_2O_3 is 23.81% at 533 K; CuO 1.56 mol%/γ-Al_2O_3, 8.24% (not given in profile); and Pt Rh Pd-1.56 mol% Cu/γ-Al_2O_3, 49.21%. The results of the activity test show that the noble metals Pt Rh Pd generate a synergistic effect with Cu. If the highly dispersed noble metal and copper are separate active components supported on the γ-Al_2O_3, then Pt Rh Pd-1.56 mol% Cu/γ-Al_2O_3 catalyst activity can not be so large. Therefore, the highly dispersed copper contributes to improve the activity of the Pt Rh Pd catalyst.

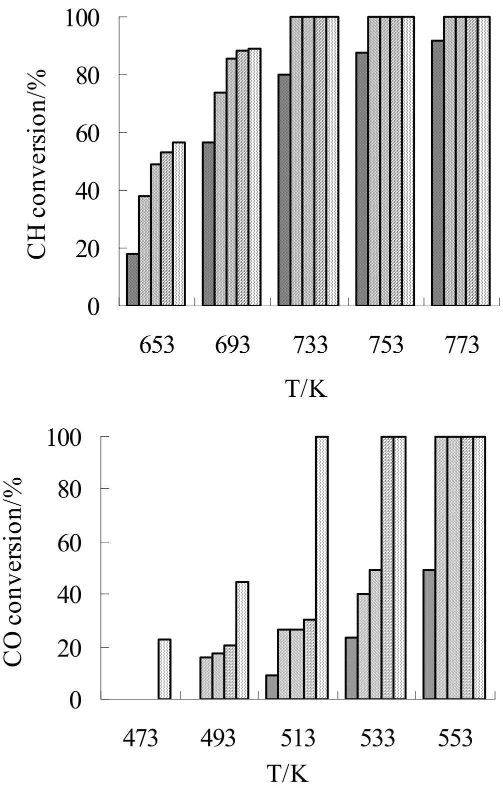

Figure 3. Effect of copper loading on the catalytic activity for CO and CH oxidation.
(Cu mol% ▩ 0.00 ▨ 0.78 ▧ 1.56 ▦ 2.34 ▯ 3.12%).

The phase interface formed by interaction had remarkable influence on catalytic activity when the distance between two phases reaches the nanometer scale [18]. The interaction between noble metal and copper may have produced the new active center, which greatly improved the catalytic activity.

The XRD of the catalysts (Figure 4) shows the characteristic diffraction peaks of the copper and noble metal did not appear in the Pt Rh Pd-1.56 mol% Cu/γ-Al_2O_3 catalyst, which indicates that the copper and noble metal are highly dispersed on the γ-Al_2O_3 support. The dispersion of noble metals in the Pt Rh Pd /γ-Al_2O_3 catalyst is 24.5%, the dispersion increase to 29.4% in Pt Rh Pd-1.56 mol% Cu/γ-Al_2O_3 catalyst. It is obviously that the addition of CuO improved the dispersion of the noble metals.

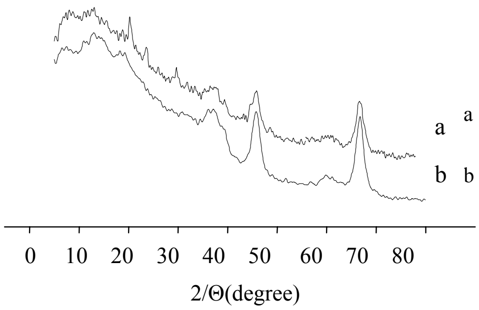

Figure 4. XRD patterns of the catalysts. a: Pt-Rh-Pd/Al_2O_3 and b: Pt-Rh-Pd-1.56% Cu/Al_2O_3.

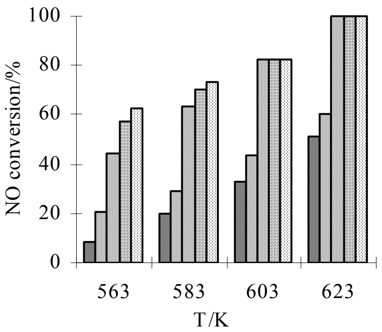

Figure 5. Effect of copper loading on the catalytic activity for NO conversion. (Cu mol%: 0.00%, 0.78%, 1.56%, 2.34%, 3.12%, respectively).

The dispersion threshold is the utmost dispersion capacity of metal on support as a monolayer. As reported, metal oxides trend to single layer dispersion on support [19], ~6.24 mol% Cu/100 m^2/g γ-aluminas support surface area [20]. In this article, γ-alumina surface area is 167 m^2/g, the dispersion threshold of Cu is 10.4 mol%, the highest content of copper on Pt Rh Pd-Cu/γ-Al_2O_3 catalyst is 3.12 mol%, smaller than the dispersion threshold of Cu. It can be concluded that catalytic activity of Pt Rh Pd-Cu /γ-Al_2O_3 increases with the increase in copper content.

It can be found from Figure 5 that the addition of copper is advantageous to the conversion of NO_x. With the increase in copper content, the activity of Pt Rh Pd-Cu/γ-Al_2O_3 catalyst rises, indicating the addition of copper could promote the reduction of the nitrogen oxide. Noble metal (especially Rh) catalysts can reduce nitrogen oxide, but Rh_2O_3 and γ-Al_2O_3 forms fused solid above 873 K [21] in the oxidizing atmosphere and the activity of Rh catalyst decreases, Rh_2O_3 and γ-Al_2O_3 interaction will weaken by the presence of copper.

Effect of copper on adsorbability over Pt Rh Pd /γ-Al₂O₃ catalyst

Pt Rh Pd/γ-Al_2O_3 and 1.56 mol% Cu/γ-Al_2O_3 catalysts produces one CO desorption peak (420 K and 357 K), respectively. Pt Rh Pd-1.56 mol% Cu/γ-Al_2O_3 catalyst produces three CO desorption peaks (Figure 6). The desorption peaks located at 420 K and 353 K, which correspond to the peaks of Pt Rh Pd /γ-Al_2O_3 and Cu/γ-Al_2O_3 catalyst, respectively, indicate that the noble metals in Pt Rh Pd-Cu /γ-Al_2O_3 do not have a totally synergistic effect with the copper, quite a few of noble metals and copper exist in the sole oxide. The new desorption peak (377 K) can be explained by the interaction between the noble metal and copper.

It can be seen from Figure 6 that there are two peaks (422 K and 359 K) in the O_2-TPD curve of Pt Rh Pd-1.56 mol% Cu/γ-Al_2O_3 catalyst, the peaks at 422 K and 359 K correspond to the desorption of the oxygen on the Pt Rh Pd/γ-Al_2O_3 and Cu/γ-Al_2O_3 catalyst, respectively. The absorption peaks area of O_2 and CO of Pt Rh Pd-1.56 mol% Cu/γ-Al_2O_3 is larger than Pt Rh Pd/γ-Al_2O_3, it could be attributed to the effect of copper on Pt Rh Pd /γ-Al_2O_3. Because some of the noble metals may have entered the bulk phase of γ-Al_2O_3 after calcination of Pt Rh Pd/γ-Al_2O_3 catalyst [22], first impregnating with copper to the followed impregnation with the noble metal in the Pt Rh Pd-Cu/γ-Al_2O_3 catalyst may result in a weaker interaction between Pt Rh Pd and γ-Al_2O_3. At the same time, copper improved dispersion of the noble metal and also improved the absorption of CO and O_2 on the Pt Rh Pd/γ-Al_2O_3catalyst.

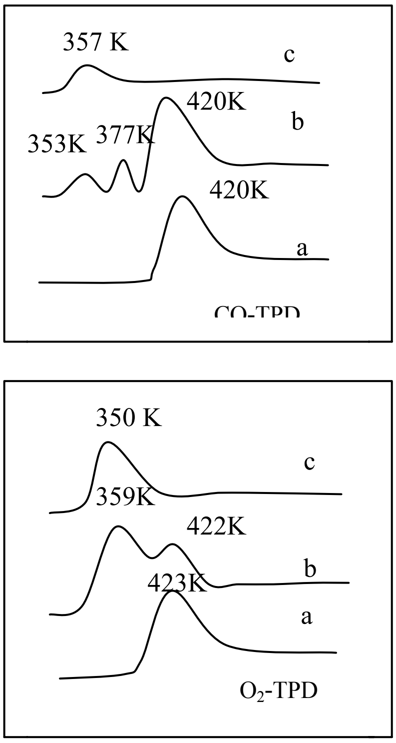

Figure 6. TPD profiles of the catalysts. a: Pt Rh Pd/Al_2O_3, b: Pt Rh Pd-1.56% Cu/Al_2O_3, c: 1.56%Cu/Al_2O_3.

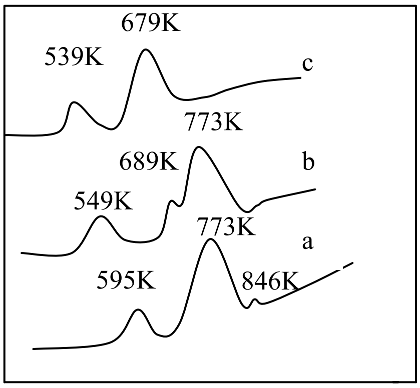

Figure 7. TPR profiles of the catalysts. a: Pt Rh Pd/Al_2O_3, b: Pt Rh Pd-1.56% Cu/Al_2O_3, c: 1.56%Cu/Al_2O_3

Effect of copper on reduction ability over Pt Rh Pd /γ-Al_2O_3 catalyst

Figure 7 shows the TPR profile of Pt Rh Pd/γ-Al_2O_3; 1.56mol% CuO/γ-Al_2O_3 and Pt Rh Pd-1.56 mol% CuO/γ-Al_2O_3 catalysts. The TPR profile of reference CuO/γ-Al_2O_3 exhibits peaks at 613 and 713 K originating from the two-step reduction of the Cu^{2+} ion to metallic copper [23]. The TPR profile of the CuO/γ-Al_2O_3 shows two peaks at about 539 and 679 K. According to the literature [24-26], the low temperature peak might be assigned to the reduction of several highly dispersed copper oxide species. The high temperature peak might be attributed to the reduction of the supported Cu^+ ions (arising from partial reduction of isolated Cu^{2+}) to Cu^0 [24, 26]. There are three peaks in the TPR curve of Pt Rh Pd/γ-Al_2O_3 and Pt Rh Pd-1.56 mol% CuO/γ-Al_2O_3 catalysts, the main reduction peak for the above two catalysts is located at 773 K. Compare with the TPR peaks at 595 K and 846 K of Pt Rh Pd/γ-Al_2O_3 catalyst, the reduction peaks of Pt Rh Pd-1.56 mol% CuO/γ-Al_2O_3 catalyst moved forward, which can be attributed to the addition of copper. It is known that there are electron holes in 4d energy level of noble metal atom; holes can accept electrons from other atoms or ion. In the course of reduction of catalyst, as a result of hydrogen spillover [27] and catalysis of noble metal, a part of transition metal oxide that migrated to the surface of noble metal will be reduced to low-valence transition metal oxide. The unsteady oxides possess a trend of transfer electron to noble metal, which changes electron state of the surface of noble metal [28]. In this way, the d electronic density of noble metals Pt Rh Pd was improved, and Pt Rh Pd-1.56 mol% CuO/γ-Al_2O_3 catalyst is easier to reduce. The increase of the dispersion also promotes the reduction of the noble metal in the catalyst.

CONCLUSION

Experimental results show that the addition of transition metal oxides (Zr, Mn, Co, Cu, Mo) are helpful in increasing activities of Pt Rh Pd/γ-Al_2O_3 catalyst, the effective order of the promoters is $CuO > ZrO_2 > Co_3O_4 > MnO_2$. Pt Rh Pd-Cu/$\gamma$-$Al_2O_3$ TWCs has a better activity for CO, CH and NO_x conversion. The copper interaction with the noble metals could change their performance for reduction and adsorption.

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