

## Precious metal-support interaction in automotive exhaust catalysts

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**Abstract:** Precious metal-support interaction plays an important role in thermal stability and catalytic performance of the automotive exhaust catalysts. The support is not only a carrier for active compounds in catalysts but also can improve the dispersion of precious metals and suppress the sintering of precious metals at high temperature; meanwhile, noble metals can also enhance the redox performance and oxygen storage capacity of support. The mechanism of metal-support interactions mainly includes electronic interaction, formation of alloy and inward diffusion of metal into the support or covered by support. The form and degree of precious metal-support interaction depend on many factors, including the content of precious metal, the species of support and metal, and preparation methods. The research results about strong metal-support interaction (SMSI) gave a theory support for developing a kind of new catalyst with excellent performance. This paper reviewed the interaction phenomenon and mechanism of precious metals (Pt, Pd, Rh) and support such as  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{CeO}_2$ -based oxides in automotive exhaust catalysts. The factors that affect SMSI and the catalysts developed by SMSI were also discussed.

**Keywords:** strong metal-support interaction; automotive exhaust catalyst; precious metal;  $\text{Al}_2\text{O}_3$ ;  $\text{CeO}_2$ -based oxides; rare earths

Recently, three-way catalyst (TWC) was widely applied in catalytic removal technology due to its excellent conversion for CO, HC and  $\text{NO}_x$ . The main components in TWCs are precious metals (PM) such as platinum (Pt), palladium (Pd), or rhodium (Rh) as the active component, and inorganic oxide such as  $\gamma$ -alumina ( $\text{Al}_2\text{O}_3$ ),  $\text{CeO}_2$ , and ceria-based composite oxides as the support. The support is not only a carrier for active compounds, but also can show catalytic activity and interact with active compositions, to influence the adsorption property and catalytic performance of catalysts.

In 1987, Tauster et al.<sup>[1]</sup> found a surprisingly strong inhibition of CO and  $\text{H}_2$  chemisorption when the group VIII precious metals supported on  $\text{TiO}_2$  after reduction at 500 °C in  $\text{H}_2$ . The characterization results showed that the inhibition of CO and  $\text{H}_2$  chemisorption was not induced by the sintering of metals, encapsulation of metals and poisoning. Thus the strong metal-support interaction (SMSI) was proposed to explain this phenomenon. From then on, the SMSI was studied by many workers. Afterwards, the decreased chemisorption of CO and  $\text{H}_2$  on Pd/ $\text{CeO}_2$ <sup>[2]</sup> was also found after high temperature reduction.

In this article, we discussed metal-support interactions between the precious metal (Pt, Pd, Rh) and the support such as  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{CeO}_2$ -based composite oxides. The interactions appear to be different significantly in form and degree due to the kind of support and precious

metal. The mechanisms of metal-support interactions: electronic interaction, formation of alloy and inward diffusion of metal into the support or covered by support were discussed. In addition, we also reviewed the factors that affect SMSI and catalyst developed by strong metal-support interaction.

### 1 Role of SMSI in three-way catalyst

Precious metal-support interaction plays an important role in catalytic performance of TWCs. The support can improve the dispersion of precious metals and suppress the sintering of noble metals at high temperature, and thus can enhance the catalytic performance and endurance ability. Farmer et al.<sup>[3]</sup> found when Ag nanoparticles supported on  $\text{CeO}_2$ , smaller metal particles were maintained by strong metal-support bonding. The Pt–O–Ce bond acted as an anchor and inhibited the sintering of Pt particles on ceria-based oxide<sup>[4]</sup>. Under the simulated exhaust gas, the effects of SMSI between Pd and  $\text{CeO}_2$  in Pd/ $\text{CeO}_2$  on the catalytic activity were investigated by XRD and CO chemisorption. It was shown that high temperature reduction could generate the SMSI of Pd/ $\text{CeO}_2$  and the SMSI could sharply improve the catalytic activity for simulated exhaust gas, and the light off temperature of CO decreased from 520 to 350 °C<sup>[2]</sup>.

Noble metals can also enhance the redox performance

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and oxygen storage capacity of support<sup>[5-8]</sup>. For example, Pt, Pd, Rh promoted the reduction of surface oxygen of CeO<sub>2</sub>, especially Rh<sup>[9]</sup>. For Pt/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, Pd/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> and Rh/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, the surface area of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> was strongly encumbered after treatments by Rh and the noble metal promoted the reduction of the support intensively compared with the metal-free Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub><sup>[5]</sup>. After three cycles of Pt(1%)/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> reduction<sup>[6]</sup>, it was displayed that Pt favoured the structural reforming of ceria-zirconia into one cubic solid solution<sup>[8]</sup>, and prevented CeAlO<sub>3</sub> formation which is harmful to the catalytic performance. TEM investigated the redox cycle of Pt(1%)/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> catalyst. It was shown that Pt particles (2–3 nm) strongly interacted with ceria, and it highly dispersed on ceria-zirconia grains with diameter between 10 and 35 nm.

However, SMSI is not always good for the catalytic performance, too strong or too weak metal-support interaction was not favorable for the catalytic activity. Liotta et al.<sup>[8]</sup> reported that SMSI were detrimental for the catalytic activity when Pt(1%)/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> was reduced at 1050 °C. At this high temperature an inward diffusion of platinum into the ceria would induce the amount of exposed metal decrease noticeably. Kenevey et al.<sup>[10]</sup> found that the presence of noble metal accelerated the de-mixing process in Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> materials, but no effect of the metal was observed for the Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> system.

## 2 Precious metal-support interaction

The metal-support interaction was evidenced by many experiments. It depends on support and metal, different support and metal will lead to different interaction. The mainly metal-support interaction in automotive exhaust catalysts is shown in Fig. 1.

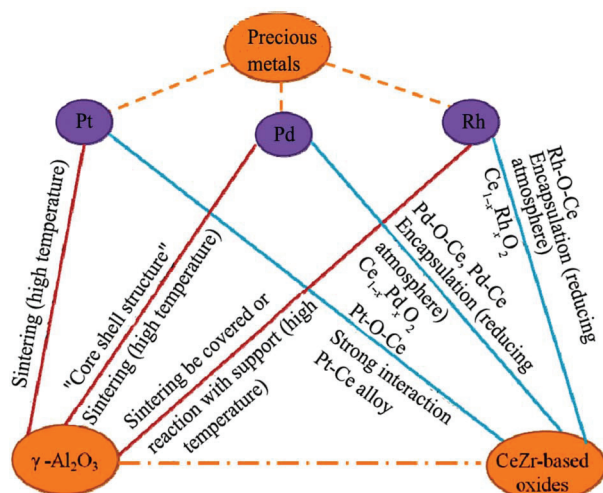


Fig. 1 Schematic diagram of metal-support interaction in automotive exhaust catalysts

### 2.1 Interaction of Pt, Pd, Rh with $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> is applied in automotive catalysts as support

due to its large surface area and high thermal stability. Identifying metal-support interactions are essential because these interactions are known to affect catalytic structure and activity significantly. To understand how metal particles bind and migrate on the surface is also important to develop accurate models to describe the processes such as metal growth as well as catalytic reactions involving both support and metal.

In the earlier studies of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, it was found that after heating in H<sub>2</sub> above 500 °C, the hydrogen adsorption capacity on Pt decreased. The lost capacity can be recovered by calcination in O<sub>2</sub> or air at 500 °C and reduced at a lower temperature (300 °C for example). It was supposed that the loss of adsorption capacity of Pt after reduction at 500 °C was due to the reversible combination of Pt with Al to form a Pt-Al alloy which was inaccessible to H<sub>2</sub>. Kuczynski et al.<sup>[11]</sup> had studied the TPR of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and found no evidence of reduction in a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support even in the presence of Pt at temperature up to 750 °C. In accordance with the results of Yao et al.<sup>[12]</sup>, Ivanova et al.<sup>[13]</sup> found that two types of the Pt and Pd particles were typically present on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, individual particles with dimensions of 1.5–3 nm and agglomerates about 100 nm in size. At low calcination temperature, Pt presented as metal cluster, such as Pt<sub>2</sub>, Pt<sub>3</sub> and Pt<sub>4</sub>, some research also evidenced this result<sup>[14]</sup>. To better understand the interactions between Pt and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, Deskins et al.<sup>[15]</sup> studied the adsorption and diffusion of a single Pt atom on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using density functional theory and found Pt binding to surface O atoms. The bonding is explained as being a combination of charge transfer between the surface and Pt atom, polarization of the metal atom, and some weak covalent bonding. At low temperature (<200 °C), the Pt atom can be trapped at certain surface regions, which could explain why the sintering process is hindered at low temperature. But at higher temperature the Pt atom is much more mobile and can move across different regions of the surface. This trapping of the Pt at local regions on the surface would have a strong effect on the formation and clustering of larger metal particles. So according to recent reports, Pt generally existed as clustering of larger metal particles on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> rather than be covered by  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The interaction of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was different from Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. According to the conclusion of Ivanova et al.<sup>[13]</sup>, for Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, the palladium particles were almost completely decorated with a thin layer of an aluminate phase and led to the formation of a so-called “core-shell structure”, depending on the calcination temperature of catalyst in the range of 450–1000 °C, the morphological form of active component was converted from the “core-shell” state to a state consisting of two phases, Pd<sup>0</sup> and PdO. With a gradual decrease ratio of Pd<sup>0</sup>/PdO, the interaction of Pd with support became weak, after

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