Enhancement of Catalytic Activity of Pt/CeO$_2$-ZrO$_2$ by Mo Addition for Diesel Exhaust CO and C$_3$H$_6$ Purification

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Abstract: A series of Pt-Mo/CeO$_2$-ZrO$_2$ diesel oxidation catalysts with different content of Mo were prepared via impregnation method. The effect of Mo promoter on catalytic activity was investigated, and the catalysts were characterized by X-ray diffraction (XRD), $H_2$ temperature-programmed reduction (TPR) and $NH_3$ temperature-programmed desorption (TRD). The catalytic activity measurements indicated that the Pt-0.5Mo/CeO$_2$-ZrO$_2$ catalyst with 0.5 wt.% of Mo addition showed obviously better catalytic performance than the Pt/CeO$_2$-ZrO$_2$ catalyst, but 1.0 wt.% and 1.5 wt.% of Mo addition decreased the catalytic activity. XRD spectra suggested that Mo promoter in Pt/CeO$_2$-ZrO$_2$ catalyst existed in a highly dispersed state. The $H_2$-TPR and $NH_3$-TPD results implied that appropriate content of Mo in Pt/CeO$_2$-ZrO$_2$ catalyst is advantageous to improve the surface strong acid sites, facilitate the dispersion of Pt particles and promote the low temperature reduction of catalyst, and therefore enhancing the catalytic activity. Therefore, this work shows that appropriate content of Mo in Pt/CeO$_2$-ZrO$_2$ catalyst can efficiently facilitate the Pt dispersion, optimize the surface acidity and low temperature reducibility and hence enhance the catalytic activity of diesel propylene and CO oxidation purification.

Keywords: Diesel oxidation catalyst; Mo promoter; Emissions purification; surface acidity; low temperature reducibility
1. Introduction

In the recent decades, atmospheric environmental pollution is one of the most serious problems, emission gases regulation of automotive has become more strict.[1] To efficiently control the auto exhaust gases, traditional internal purification technology combining aftertreatment catalysts was used to accomplish regulation limit.[2] The lean-burn conditions of diesel engines caused the low emission temperature and miscellaneous air pollutants. Nowadays, several diesel emission aftertreatment systems were carried out to purify diesel exhaust.[3, 4] In these aftertreatment systems, diesel oxidation catalyst was one of the simplest catalysts and have been utilized the longest, which was mainly used to reduce CO and unburned hydrocarbons emissions.[1]

Generally, diesel oxidation catalysts were prepared by supporting noble metals (such as Pt, Pd etc.) on the CeO$_2$, ZrO$_2$, Al$_2$O$_3$ and their mixed oxides.[5, 6] While, the commercial application of diesel oxidation catalysts led to the consuming of considerable amount of noble metals, which was considered disadvantageous for the promotion of diesel oxidation catalysts. The introduction of catalyst promoter provided an important and effective means to reduce noble metal consumption and enhance catalytic performance.[7, 8] Transition metal oxides (Sn, W etc.) were widely used as a dispersion promoter for Pt based catalyst, due to the transition metal oxides moderator interaction which effects between Pt and supported and modify the metal particle size.[9-12] And Burch et. al. have reported that metal oxides promoters have a significant effect on the activity of Pt based catalysts under lean-burn conditions.[13] Moreover, researches have attested that Mo oxides can form a solid solution with Pt[14] and facilitate the dispersion of Pt particles[15]. However, the effect of Mo oxides on the activity of Pt/CeO$_2$-ZrO$_2$ catalyst for diesel exhaust purification was not thoroughly investigated. Considering all of this, Mo was added in Pt/CeO$_2$-ZrO$_2$ diesel oxidation catalyst, and the effect of Mo oxides on catalytic activity of diesel C$_3$H$_6$ and CO oxidation purification was investigated.

2. Materials and Methods

2.1 Materials

Ammonium hydroxide, Ce(NO)$_3$·6H$_2$O and ZrOCO$_3$·2H$_2$O were purchased from Chengdu Kelong Chemical Reagent Factory (China), (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O was purchased from Tianjin Chemical Reagent Factory No. 4 (China), Nitrite platinum (Pt(NO$_3$)$_2$) was purchased from Heraeus, all the chemicals were of analytical grade and used without further purification.

2.2 Catalysts

CeO$_2$-ZrO$_2$ mixed oxides were synthesized by co-precipitation. Calculated amount of Ce(NO)$_3$·6H$_2$O and ZrOCO$_3$·2H$_2$O were slowly mixed with NH$_3$·H$_2$O solutions under stirring. The resulting precipitate was washed by deionized water, after filtered and dried at 120 °C. The CeO$_2$-ZrO$_2$ mixed oxides powder was obtained by calcined the powder at 600 °C for 3 hours under air flow, and then used as catalyst support.

A series of Pt-Mo/CeO$_2$-ZrO$_2$ catalysts with different Mo content were prepared by impregnating the CeO$_2$-ZrO$_2$ support with Pt(NO$_3$)$_2$ and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O solutions. After drying at 120 °C overnight and baking at 500 °C for 3 hours the Pt-Mo/CeO$_2$-ZrO$_2$ catalyst powders were obtained. All of the Pt-Mo/CeO$_2$-ZrO$_2$ catalysts contain 1 wt.% Pt and different Mo. The catalyst containing 0 wt.%, 0.5 wt.%, 1.0 wt.% and 1.5 wt.%
of Mo were marked as Pt-Mo/CeO$_2$-ZrO$_2$, Pt-0.5Mo/CeO$_2$-ZrO$_2$, Pt-1.0Mo/CeO$_2$-ZrO$_2$ and Pt-1.5Mo/CeO$_2$-ZrO$_2$, respectively.

2.3 Activity Measurements

The activity measurement was performed on a fixed-bed flow reactor. About 0.35 g catalyst was placed in a quartz reactor, and then the simulative diesel exhaust gases were flowed through the catalyst. The simulative diesel exhaust gases containing: 1000 ppm CO, 500 ppm C$_3$H$_6$, 500 ppm NO, 6% CO$_2$, 10% O$_2$, 10% water vapor, 100 ppm SO$_2$, and N$_2$ balance at a gas hourly space velocity of 30000 h$^{-1}$. CO concentration in the inlet and outlet gases was measured by an automotive emission analyzer (FGA-4100, Foshan Analytical Instruments, China) and C$_3$H$_6$ was analyzed by an online gas chromatograph (GC2000, Shanghai Analysis Instruments, China) with flame ionization detector (FID). Before the testing, all catalysts were pre-treated at 500 °C for 3 hours in the reaction gases conditions.

2.4 Characterizations

Powder X-ray diffraction (XRD) was detected on a DX-1000 diffractometer (Dandong Instruments, China) with Cu Kα ($\lambda = 0.1541$ nm) radiation.

Hydrogen-temperature programmed reduction (H$_2$-TPR) was performed on a chemical adsorption instrument TP-5050 (Xianquan Instrument, China). About 0.1 g of catalyst was placed in a quartz tube and then pretreated at 25 mL/min N$_2$ flow at 450 °C for 1 h, after cooling down to room temperature, the catalyst was heated from room temperature to 450 °C with a rate of 10 °C/min at 20 mL/min flowing gas mixture of 5 vol.%H$_2$-N$_2$. The H$_2$ consumption was monitored by a thermal conductivity detector (TCD).

NH$_3$-temperature programmed desorption (NH$_3$-TPD) was carried on a chemical adsorption instrument TP-5050 (Xianquan Instrument, China). About 0.1 g catalyst was pretreated under Ar flow with a rate of 30 mL/min at 450 °C for 1 h, and then adsorbed the mixture gases of 2 vol.% NH$_3$-Ar at 80 °C for 1 h, after isothermal desorption under Ar flow at 80 °C until no NH$_3$ was detected, the temperature programmed desorption in Ar from 80 °C to 750 °C with 10 °C/min was finally carried. The NH$_3$ concentration was monitored by a thermal conductivity detector (TCD).
3. Results and Discussion

3.1 Activity

Fig. 1 (a) CO and (b) C$_3$H$_6$ conversion over the Pt/CeO$_2$-ZrO$_2$, Pt-0.5Mo/CeO$_2$-ZrO$_2$, Pt-1.0Mo/CeO$_2$-ZrO$_2$ and Pt-1.5Mo/CeO$_2$-ZrO$_2$ catalysts

The catalytic performances of as-prepared catalysts for CO and C$_3$H$_6$ oxidation were shown in Fig. 1. It can be seen that CO and C$_3$H$_6$ conversion on catalysts increased with the raising of temperature. The Pt-0.5Mo/CeO$_2$-ZrO$_2$ catalyst with 0.5 wt.% of Mo promoter showed the best activity for CO and C$_3$H$_6$ oxidation. However, a much more content of Mo additive was adverse to the reactivity of Pt/CeO$_2$-ZrO$_2$ catalyst. The Pt-1.0Mo/CeO$_2$-ZrO$_2$ and Pt-1.5Mo/CeO$_2$-ZrO$_2$ catalyst displayed worse activity than that of Pt/CeO$_2$-ZrO$_2$ catalyst.

Table 1 The light-off temperature ($T_{50}$) and complete combustion temperature ($T_{90}$) of C$_3$H$_6$ and CO on catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO</th>
<th></th>
<th>C$_3$H$_6$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{50}$/°C</td>
<td>$T_{90}$/°C</td>
<td>$T_{50}$/°C</td>
<td>$T_{90}$/°C</td>
</tr>
<tr>
<td>Pt/CeO$_2$-ZrO$_2$</td>
<td>253</td>
<td>274</td>
<td>267</td>
<td>297</td>
</tr>
<tr>
<td>Pt-0.5Mo/CeO$_2$-ZrO$_2$</td>
<td>240</td>
<td>252</td>
<td>243</td>
<td>253</td>
</tr>
<tr>
<td>Pt-1.0Mo/CeO$_2$-ZrO$_2$</td>
<td>272</td>
<td>296</td>
<td>273</td>
<td>296</td>
</tr>
<tr>
<td>Pt-1.5Mo/CeO$_2$-ZrO$_2$</td>
<td>268</td>
<td>291</td>
<td>272</td>
<td>292</td>
</tr>
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The light-off temperature ($T_{50}$, the temperature that reactant conversion reaches 50%) and complete combustion temperature ($T_{90}$, the temperature that reactant conversion reaches 90%) of each catalyst were listed in Table 1. For CO oxidation, the $T_{50}$ of Pt/CeO$_2$-ZrO$_2$ catalyst was 253 °C; the addition of 0.5 wt.% of Mo promoter led to a $T_{50}$ decrease of about 13 °C; and the $T_{50}$ of Pt-1.0Mo/CeO$_2$-ZrO$_2$ and Pt-1.5Mo/CeO$_2$-ZrO$_2$ catalysts were 272 °C and 268 °C, respectively, which is worse than the unmodified Pt/CeO$_2$-ZrO$_2$ catalyst. The catalytic performance for C$_3$H$_6$ oxidation showed the same trend, the $T_{50}$ of Pt/CeO$_2$-ZrO$_2$ for C$_3$H$_6$ oxidation was 267 °C, and that of Pt-0.5Mo/CeO$_2$-ZrO$_2$ was 243 °C; for the Pt-1.0Mo/CeO$_2$-ZrO$_2$ and Pt-1.5Mo/CeO$_2$-ZrO$_2$ catalysts, the $T_{50}$ of C$_3$H$_6$ were 273 °C and 272 °C, respectively. And therefore it is clear
that appropriate amount of Mo additive in the Pt/CeO$_2$-ZrO$_2$ catalyst is conducive to the improvement of catalytic activity, however excessive amount of Mo addition will cause the deactivation of catalysts. To investigate the reasons why appropriate amount of Mo additive can improve the catalytic activity of Pt/CeO$_2$-ZrO$_2$ catalyst, several characterizations were carried out.

3.2 Catalyst Characterization

3.2.1 XRD

![XRD patterns of catalysts](image)

**Fig. 2** XRD patterns of the Pt/CeO$_2$-ZrO$_2$, Pt-0.5Mo/CeO$_2$-ZrO$_2$, Pt-1.0Mo/CeO$_2$-ZrO$_2$ and Pt-1.5Mo/CeO$_2$-ZrO$_2$ catalysts

Fig. 2 shows the XRD patterns of catalysts. Four distinct peaks were observed in all samples. The peak at about 29.3° can be ascribed to the (101) plane of Zr$_{0.5}$Ce$_{0.5}$O$_2$. The broad peak locating at about 34° can be attributed to Zr$_{0.5}$Ce$_{0.5}$O$_2$ (002) and (110). The multiple peak at about 48° were assigned to the Zr$_{0.5}$Ce$_{0.5}$O$_2$ (112) and (200) plane. The superposed characteristic peaks of Zr$_{0.5}$Ce$_{0.5}$O$_2$ (103) and (211) plane ($2\theta = 57.7°$ and 58°) were detected at the $2\theta$ of about 55-60°. Additionally, no diffraction signal of Pt or Mo were detected in the XRD patterns, which infer that the Pt and Mo were not formed multiple crystal, or at least the crystal grains were too small to form multiple faces.[16] In any case, it can be safely concluded that Pt and Mo were highly dispersed on the surface of catalysts.
3.2.2 TPD

![Fig. 2 NH₃-TPD profiles of the Pt/CeO₂-ZrO₂, Pt-0.5Mo/CeO₂-ZrO₂, Pt-1.0Mo/CeO₂-ZrO₂ and Pt-1.5Mo/CeO₂-ZrO₂ catalysts.](image)

The surface acidic strength of catalysts can fundamentally affect the adsorption of hydrocarbons, and hence play a crucial role in the catalytic activity of hydrocarbon combustion. The surface acidity of catalysts were detected by NH₃-TPD technique. As is shown in Fig. 2, all the samples exhibited an apparent NH₃ desorption peak at about 220 °C implying the weak acid sites of catalysts; and the addition of Mo have bring about a distinct peak at about 520 °C, which can be attributed to the strong acid species. The strong acid peak of Pt-0.5Mo/CeO₂-ZrO₂ catalyst was the most of this series; and the strong acid peak decreased and weak acid peak increased gradually with the further increase of Mo additive loading; which indicate that suitable amount of Mo addition can efficiently enhance the strong acid sites of Pt/CeO₂-ZrO₂ catalyst, superfluous amount of Mo will improve the weak acid sites. Due to the fact that Mo oxide species can form a solid solution with Pt, the formation of Pt-Mo solid solution may results in the arising of strong acid sites, however excess Mo may imbed the Pt particle and therefore decrease the strong acid sites. Since suitable strong acidity of catalysts were beneficial for the surface adsorption of propylene and CO, and hence improving the catalytic combustion activity. It can be inferred that suitable amount of Mo promoter in the Pt/CeO₂-ZrO₂ catalyst can play a crucial role for enhancing the surface acidity of catalyst and hence improving the catalytic propylene and CO oxidation activity.
3.2.3 TPR

![Graph]

**Fig. 3** H$_2$-TPR profiles of the Pt/CeO$_2$-ZrO$_2$, Pt-0.5Mo/CeO$_2$-ZrO$_2$, Pt-1.0Mo/CeO$_2$-ZrO$_2$ and Pt-1.5Mo/CeO$_2$-ZrO$_2$ catalysts

The low temperature reduction property of catalyst is closely related to the activity.$^{[6,20]}$ The reducibility of catalyst was evaluated by H$_2$-TPR, as presented in Fig.3. Pt/CeO$_2$-ZrO$_2$ catalyst showed a clear peak at about 100 °C, which can be attributed to the reduction of Pt and surface of support materials which showed metal-support interaction;$^{[6,19,21]}$ the reduction peak after 300 °C was mainly because of the reduction of CeO$_2$-ZrO$_2$ support materials,$^{[6]}$ and it was not discussed detailedly due to the catalytic CO and C$_3$H$_6$ oxidation of catalyst were before 300 °C. Due to 0.5 wt.% of Mo addition, Pt-0.5Mo/CeO$_2$-ZrO$_2$ catalyst exhibited a larger reduction peak at a lower temperature (begin at about 30 °C) than other catalysts. This is because Mo oxides can facilitate the dispersion of Pt particles,$^{[15]}$ the smaller and more uniformly dispersed Pt particles were more easily reduced at lower temperature and hence more easily involved in the catalytic reactions at lower temperature and showed better activity. More amount of Mo addition (1.0 wt.% and 1.5 wt%) increased the peak area but obviously postponed the reduction temperature, which may ascribed to the surface Pt particles were imbedded by Pt-Mo alloys. It can be seen that appropriate amount of Mo additive can improve the low temperature reducibility of Pt/CeO$_2$-ZrO$_2$ catalyst, which is advantageous to the low temperature activity; but excess addition of Mo can only be counterproductive.

4. Conclusions

From the above results, it is feasible to indicate that suitable amount of Mo additive in Pt/CeO$_2$-ZrO$_2$ catalyst is beneficial for enhancing the catalytic activity of diesel C$_3$H$_6$ and CO oxidation, but excess addition of Mo can only be counterproductive. Mo additive amount of 0.5 wt.% is the optimal proportion. Mo promoter in Pt/CeO$_2$-ZrO$_2$ catalyst have existed in a highly dispersed state. Appropriate amount of Mo in Pt/CeO$_2$-ZrO$_2$ is advantageous to improve the surface strong acid sites, facilitate the dispersion of Pt particles and promote the low temperature reduction of catalyst, and therefore enhancing the catalytic activity. Excessively much more...
amount of Mo addition will decrease the catalytic performances, which probably because of the surface Pt particles were imbedded by Pt-Mo solid solution.

Acknowledgements
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References


