

Effect of Platinum Precursor Type on Activity of Pt/CeO₂ catalyst in C₃H₈ and CO Oxidation

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Abstract: Noble metal precursor type has been found to affect the strong metal-support interaction and catalytic activity. Here, the effect of platinum precursor type of Pt/CeO₂ catalyst on the catalytic activity of C₃H₈ and CO oxidation was investigated in this work. The catalytic activity measurements show that the chlorine-free Pt/CeO₂(Pt(NO₃)₂) catalyst with Pt(NO₃)₂ precursor showed better catalytic activity than the chlorine-free Pt/CeO₂((EA)₂Pt(OH)₆) catalyst with (EA)₂Pt(OH)₆ precursor; moreover, the activity of chlorine-free Pt/CeO₂ catalysts were obviously superior than that of the chlorinated Pt/CeO₂(H₂PtCl₆) catalyst with platinum precursor of H₂PtCl₆, which because of the presence of chloride ions resulting from H₂PtCl₆ precursor increased the formation of surface Ce-O-Cl species and diminished the promoter effect of ceria support. The H₂-temperature programmed reduction results indicate that, the Pt(NO₃)₂ precursor exhibited stronger metal-support interaction with CeO₂ support than the (EA)₂Pt(OH)₆ precursor, and hence the Pt/CeO₂(Pt(NO₃)₂) showed lower reduction temperature and better catalytic behaviors than the Pt/CeO₂((EA)₂Pt(OH)₆) catalyst.

Keywords: Diesel oxidation catalyst; Pt precursor; chlorine-free Pt/CeO₂ catalyst; Emissions purification

1. Introduction

Cerium dioxide was widely used in heterogeneous catalysis as a support for platinum group metals. And its applications as three way catalyst for removing the air pollutants from gasoline vehicles^[1, 2] and oxidation catalyst for purifying unburned hydrocarbons and CO in diesel exhaust emissions^[3, 4] were gradually applied. The gasoline vehicular exhaust gases could be efficiently purified by three way catalyst, however, lean-burn diesel engines caused the low emission temperature, excess oxygen and miscellaneous air pollutants, and three way catalyst was not able to efficiently purify the diesel exhaust. Recent decades, diesel exhaust gases were controlled by several kinds of complex aftertreatment systems.^[5, 6] In these aftertreatment systems, Pt/CeO₂ was generally used as diesel oxidation catalyst and mainly applied to remove CO and unburned hydrocarbons in diesel emissions.^[7]

While, the consumption of noble metals caused by commercial application of diesel oxidation catalysts was considered disadvantageous for the promotion of diesel oxidation catalysts. Recently, the metal-support interaction has been used to modify the catalytic performance of noble metal supported catalyst and reduce noble metal consumption. For instance, noble metal platinum-ceria interaction induced after reduction strongly modified the catalytic behavior of the Pt catalyst, and this phenomenon was widely researched and called strong metal-support interaction (SMSI) effect.^[8-10] And noble metal precursor type has also been found to affect the SMSI effect and catalytic activity.^[9, 11] In this sense, Chloroplatinic acid (H₂PtCl₆) as a chlorinated precursor, Nitrite platinum Pt(NO₃)₂ and (EA)₂Pt(OH)₆ as chlorine-free precursors were used to prepare Pt/CeO₂ catalyst and the effect on catalytic behavior for diesel exhaust C₃H₈ and CO oxidation was investigated in this work.

2. Materials and Methods

2.1 Materials

Ammonium hydroxide and Ce(NO₃)₃·6H₂O were purchased from Chengdu Kelong Chemical Reagent Factory (China), Chloroplatinic acid H₂PtCl₆, (EA)₂Pt(OH)₆ and Nitrite platinum Pt(NO₃)₂ were purchased from Heraeus. All the chemicals were of analytical grade and used without further purification.

2.2 Catalysts

CeO₂ support was prepared by co-precipitation. Calculated amount of Ce(NO₃)₃·6H₂O was slowly mixed with NH₃·H₂O solutions under stirring. The resulting precipitate was washed by de-ionized water several times, after filtered and dried at 120 °C. The obtained powder was calcined at 600 °C for 3 hours under air flow, then CeO₂ support was obtained and used as catalyst support.

The Pt/CeO₂ catalysts with different Pt precursor type were prepared by impregnating the CeO₂ support with H₂PtCl₆ or (EA)₂Pt(OH)₆ or Pt(NO₃)₂ solutions, respectively. After drying at 120 °C overnight and baking at 500 °C for 3 hours the Pt/CeO₂ catalyst powders were obtained. All of the catalysts contain 1 wt.% Pt. The catalyst using H₂PtCl₆ precursor was marked as Pt/CeO₂(H₂PtCl₆), the catalyst using (EA)₂Pt(OH)₆ precursor was marked as Pt/CeO₂((EA)₂Pt(OH)₆), and the catalyst using Pt(NO₃)₂ precursor was marked as Pt/CeO₂(Pt(NO₃)₂).

2.3 Activity tests

The catalytic behavior measurement was tested on a fixed-bed flow reactor. About 0.35 g catalyst was placed in a quartz tube reactor and then flowed by the simulative diesel exhaust gases: 1000 ppm CO, 500 ppm C₃H₈, 500 ppm NO, 6% CO₂, 10% O₂, 10% water vapor, and N₂ 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 C₃H₈ 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

Hydrogen-temperature programmed reduction (H₂-TPR) was carried on a chemical adsorption instrument TP-5050 (Xianquan Instrument, China). About 0.1 g catalyst was placed in the quartz tube reactor and then pretreated at 450 °C for 1 h under 25 mL/min N₂ flow, 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.%H₂-N₂. The H₂ consumption was monitored by a thermal conductivity detector (TCD).

3. Results and Discussion

3.1 Activity

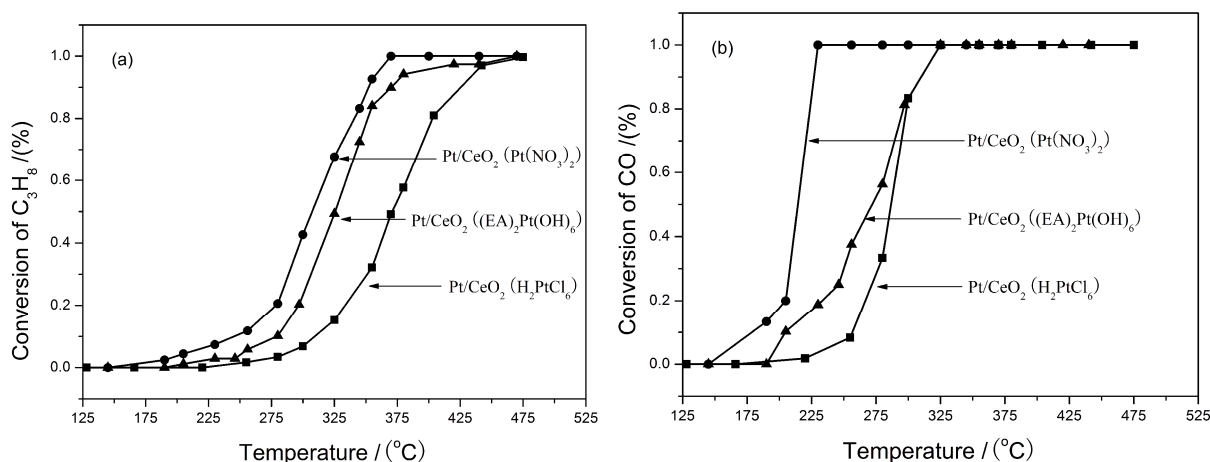


Fig. 1 (a) C₃H₈ and (b) CO conversion over the Pt/CeO₂(H₂PtCl₆), Pt/CeO₂((EA)₂Pt(OH)₆) and Pt/CeO₂(Pt(NO₃)₂) catalysts

The catalytic performances of catalysts for C₃H₈ and CO oxidation were shown in Fig. 1. It can be seen that the oxidation conversion of C₃H₈ and CO on catalysts increased with the raising of temperature. The chlorine-free catalyst Pt/CeO₂(Pt(NO₃)₂) showed the best activity for C₃H₈ and CO oxidation. In the meanwhile, Pt/CeO₂((EA)₂Pt(OH)₆) chlorine-free catalyst also showed better activity than the chlorinated catalyst

Pt/CeO₂(H₂PtCl₆). This trend implied that chlorine-free Pt/CeO₂ catalysts possess better catalytic activity for C₃H₈ and CO oxidation than the chlorinated Pt/CeO₂ catalyst. The catalytic behavior details, light-off temperature (T₅₀, the temperature that reactant conversion reaches 50%) and complete combustion temperature (T₉₀, the temperature that reactant conversion reaches 90%), of all catalysts were listed in Table 1.

Table 1 The light-off temperature (T₅₀) and complete combustion temperature (T₉₀) of CO and C₃H₈ on Pt/CeO₂(H₂PtCl₆), Pt/CeO₂((EA)₂Pt(OH)₆) and Pt/CeO₂(Pt(NO₃)₂) catalysts

Catalysts	CO		C ₃ H ₈	
	T ₅₀ /°C	T ₉₀ /°C	T ₅₀ /°C	T ₉₀ /°C
Pt/CeO ₂ (H ₂ PtCl ₆)	287	310	371	425
Pt/CeO ₂ ((EA) ₂ Pt(OH) ₆)	271	310	326	370
Pt/CeO ₂ (Pt(NO ₃) ₂)	214	226	307	353

As is shown in Table 1, the light-off temperature (T₅₀) of CO oxidation on Pt/CeO₂(H₂PtCl₆), Pt/CeO₂((EA)₂Pt(OH)₆) and Pt/CeO₂(Pt(NO₃)₂) were 287 °C, 271 °C and 214 °C, respectively. It can be seen that the chlorine-free Pt/CeO₂(Pt(NO₃)₂) catalyst showed better activity than the chlorine-free Pt/CeO₂((EA)₂Pt(OH)₆) catalyst; meanwhile, the chlorine-free Pt/CeO₂ catalysts (both Pt/CeO₂(Pt(NO₃)₂) and Pt/CeO₂((EA)₂Pt(OH)₆)) showed obviously better performance than the chlorinated Pt/CeO₂(H₂PtCl₆) catalyst. The data of complete combustion temperature (T₉₀) for all catalysts showed the same trend.

For C₃H₈ oxidation, the the light-off temperature (T₅₀) of Pt/CeO₂(H₂PtCl₆), Pt/CeO₂((EA)₂Pt(OH)₆) and Pt/CeO₂(Pt(NO₃)₂) were 371 °C, 326 °C and 307 °C, respectively. It is clear that the activity of chlorinated Pt/CeO₂(H₂PtCl₆) catalyst was obviously inferiorer than that of the chlorine-free Pt/CeO₂(Pt(NO₃)₂) and Pt/CeO₂((EA)₂Pt(OH)₆) catalyst, and the Pt/CeO₂(Pt(NO₃)₂) catalyst showed better activity than Pt/CeO₂((EA)₂Pt(OH)₆). And the scientific trend of complete combustion temperature (T₉₀) for C₃H₈ oxidation showed the same trend.

Generally, the catalytic activity of chlorine-free Pt/CeO₂ catalysts were significantly superior than that of the chlorinated Pt/CeO₂(H₂PtCl₆) catalyst, which may because of that the presence of chloride ions increased the formation of surface Ce-O-Cl species and hence diminished the promoter effect of ceria support.^[9] The chlorine-free Pt/CeO₂(Pt(NO₃)₂) showed better catalytic activity than the chlorine-free Pt/CeO₂((EA)₂Pt(OH)₆) catalyst, which may caused by that the different platinum precursors played different effects on the redox properties of metal-support interface and ceria support.^[11] To investigate the redox properties of as-prepared catalysts, H₂-temperature programmed reaction (H₂-TPR) was carried out.

3.2 TPR

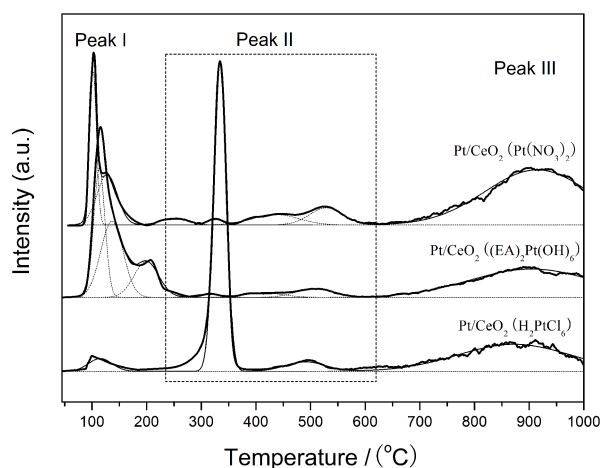


Fig. 2 H₂-TPR profiles of the Pt/CeO₂(H₂PtCl₆), Pt/CeO₂((EA)₂Pt(OH)₆) and Pt/CeO₂(Pt(NO₃)₂) catalysts

The redox properties of catalysts were evaluated by H₂-TPR, and presented in Fig.2, due to the low temperature redox property of catalyst is closely related to the activity.^[12, 13] As is shown in Fig. 2, all catalysts showed three multiple peaks, the peak I was between 100 °C and 200 °C, which can be attributed to the reduction of Pt and surface of support materials which showed metal-support interaction.^[13-15] The peak II, at about 250 °C-600 °C, was mainly because of the reduction of surface CeO₂ materials.^[13] The reduction peak III, after 600 °C, was caused by the reduction of bulk CeO₂ support materials.^[16] The reduction temperature and reduction peak area were listed in Table 2.

Table 2 The reduction temperature and reduction peak area of Pt/CeO₂(H₂PtCl₆), Pt/CeO₂((EA)₂Pt(OH)₆) and Pt/CeO₂(Pt(NO₃)₂) catalysts

Catalysts	Peak I		Peak II		Peak III	
	Temp. (°C)	Area (a.u.)	Temp. (°C)	Area (a.u.)	Temp. (°C)	Area (a.u.)
Pt/CeO ₂ (H ₂ PtCl ₆)	115	106	334	1369	872	1066
			490	133		
Pt/CeO ₂ ((EA) ₂ Pt(OH) ₆)	113	503	310	29	904	1218
	136	594	414	62		
	199	309	508	114		
Pt/CeO ₂ (Pt(NO ₃) ₂)			251	60	914	1992
	102	357	325	26		
			435	167		
	128	353	529	197		

As is presented in Table 2, the temperature of peak I of Pt/CeO₂(H₂PtCl₆) catalyst was 115 °C, and the peak area was 106; the temperature of peak II 334 °C with peak area of 1369, and the area of bulk CeO₂ reduction was 1066; which can be suggested that the presence of H₂PtCl₆ obviously promoted the surface CeO₂ reduction,

however the promotional effect of low temperature reduction of surface CeO_2 with strong metal-support interaction (SMSI) was not particularly distinct. For the $\text{Pt/CeO}_2((\text{EA})_2\text{Pt}(\text{OH})_6)$ catalyst, the area of low temperature reduction peak I, between 113 °C and 199 °C, was about 1406; and the peak area of peak II was about 205; which can be inferred that nearly all of the surface CeO_2 in the chlorine-free $\text{Pt/CeO}_2((\text{EA})_2\text{Pt}(\text{OH})_6)$ showed strong metal-support interaction (SMSI) effect. For the $\text{Pt/CeO}_2(\text{Pt}(\text{NO}_3)_2)$ catalyst, the low temperature reduction peak I at about 102 °C with reduction peak area of 357, it was lower than that of $\text{Pt/CeO}_2((\text{EA})_2\text{Pt}(\text{OH})_6)$ catalyst (113 °C), which implied that the $\text{Pt/CeO}_2(\text{Pt}(\text{NO}_3)_2)$ catalyst was more easily involved in reaction than the $\text{Pt/CeO}_2((\text{EA})_2\text{Pt}(\text{OH})_6)$ catalyst under lower temperature and hence further promote the low temperature reactions.

Generally, the presence of Pt could efficiently promoted the reduction of CeO_2 materials and hence enhanced the activity of CeO_2 based catalyst. The strong metal-support interaction (SMSI) effect of chlorinated $\text{Pt/CeO}_2(\text{H}_2\text{PtCl}_6)$ catalyst with H_2PtCl_6 precursor was relatively weak, which may because of that the presence of chloride ions increased the formation of surface Ce-O-Cl species and hence diminished the promoter effect of ceria support.^[9] And for the chlorine-free catalysts, $\text{Pt/CeO}_2(\text{Pt}(\text{NO}_3)_2)$ with $\text{Pt}(\text{NO}_3)_2$ precursor showed lower reduction temperature than the $\text{Pt/CeO}_2((\text{EA})_2\text{Pt}(\text{OH})_6)$ catalyst with $(\text{EA})_2\text{Pt}(\text{OH})_6$ precursor, which indicated that different platinum precursor of Pt/CeO_2 catalyst exhibited different strong metal-support interaction (SMSI) effect and hence affected the low temperature catalytic activity.

4. Conclusions

Based on the above mentioned results, it can be indicate that the catalytic activity of Pt/CeO_2 catalyst for C_3H_8 and CO oxidation was significantly affected by platinum precursor type. The activity of chlorine-free Pt/CeO_2 catalysts with platinum precursor of $(\text{EA})_2\text{Pt}(\text{OH})_6$ or $\text{Pt}(\text{NO}_3)_2$ were obviously superior than that of the chlorinated $\text{Pt/CeO}_2(\text{H}_2\text{PtCl}_6)$ catalyst with platinum precursor of H_2PtCl_6 , which mainly because of the presence of chloride ions increased the formation of surface Ce-O-Cl species and hence diminished the promoter effect of ceria support. And the chlorine-free $\text{Pt/CeO}_2(\text{Pt}(\text{NO}_3)_2)$ showed better catalytic activity than chlorine-free $\text{Pt/CeO}_2((\text{EA})_2\text{Pt}(\text{OH})_6)$ catalyst, which caused by that the $\text{Pt/CeO}_2(\text{Pt}(\text{NO}_3)_2)$ catalyst with $\text{Pt}(\text{NO}_3)_2$ precursor exhibited stronger metal-support interaction and lower reduction temperature than the $\text{Pt/CeO}_2((\text{EA})_2\text{Pt}(\text{OH})_6)$ catalyst with $(\text{EA})_2\text{Pt}(\text{OH})_6$ precursor, and hence better catalytic behaviors.

Acknowledgements

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References

- [1] J. Kašpar, P. Fornasiero, M. Graziani, Use of CeO₂-based oxides in the three-way catalysis, *Catal Today*, 50 (1999) 285-298.
- [2] Y. Matsuzono, K. Kuroki, T. Nishi, N. Suzuki, T. Yamada, T. Hirota, G. Zhang, Development of Advanced and Low PGM TWC System for LEV2 PZ EV and LEV3 SULEV30, SAE Technical Paper, 2012-01-1242 (2012).
- [3] A. Trovarelli, Catalytic properties of ceria and CeO₂-containing materials, *Catalysis Reviews*, 38 (1996) 439-520.
- [4] T. Kanerva, V. Kröger, K. Rahkamaa-Tolonen, M. Vippola, T. Lepistö, R. Keiski, Structural changes in air aged and poisoned diesel catalysts, *Top Catal*, 45 (2007) 137-142.
- [5] K. Hallstrom, J.M. Schiavon, Euro IV and V Diesel Emission Control System Review, SAE Technical Paper, 2007-01-2617 (2007).
- [6] H. Ueno, T. Furutani, T. Nagami, N. Aono, H. Goshima, K. Kasahara, Development of catalyst for diesel engine, SAE Technical Paper, 980195 (1998).
- [7] T. Johnson, Vehicular Emissions in Review, SAE Technical Paper, 2016-01-0919 (2016).
- [8] S. Bernal, J. Calvino, M. Cauqui, J. Gatica, C. Larese, J.P. Omil, J. Pintado, Some recent results on metal/support interaction effects in NM/CeO₂ (NM: noble metal) catalysts, *Catal Today*, 50 (1999) 175-206.
- [9] J. Silvestre-Albero, F. Coloma, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, Effect of the presence of chlorine in bimetallic PtZn/CeO₂ catalysts for the vapor-phase hydrogenation of crotonaldehyde, *Applied Catalysis A: General*, 304 (2006) 159-167.
- [10] A. Bruix, J.A. Rodriguez, P.J. Ramirez, S.D. Senanayake, J. Evans, J.B. Park, D. Stacchiola, P. Liu, J. Hrbek, F. Illas, A New Type of Strong Metal–Support Interaction and the Production of H₂ through the Transformation of Water on Pt/CeO₂ (111) and Pt/CeO_x/TiO₂ (110) Catalysts, *Journal of the American Chemical Society*, 134 (2012) 8968-8974.
- [11] C.O. Depboylu, S. Yilmaz, S. Akkurt, Effects of Catalyst Precursor Type and Preparation Conditions, and Solvent Type on Activity and Selectivity of Pt/SiO₂ Catalyst in Citral Hydrogenation, *Int J Chem React Eng*, 9 (2011).
- [12] K. Sun, W. Lu, M. Wang, X. Xu, Characterization and catalytic performances of La doped Pd/CeO₂ catalysts for methanol decomposition, *Applied Catalysis A: General*, 268 (2004) 107-113.
- [13] Z.-Z. Yang, Y. Yang, M. Zhao, M.-C. Gong, Y.-Q. Chen, Enhanced Sulfur Resistance of Pt-Pd/CeO₂-ZrO₂-Al₂O₃ Commercial Diesel Oxidation Catalyst by SiO₂ Surface Cladding, *Acta Phys-Chim Sin*, 30 (2014) 1187-1193.
- [14] Q. Tong, A. Zong, W. Gong, L. Yu, Y. Fan, Rhenium-promoted Pt/WO₃/ZrO₂: an efficient catalyst for aqueous glycerol hydrogenolysis under reduced H₂ pressure, *Rsc Adv*, 6 (2016) 86663-86672.
- [15] M.-F. Luo, Z.-Y. Hou, X.-X. Yuan, X.-M. Zheng, Characterization study of CeO₂ supported Pd catalyst for low-temperature carbon monoxide oxidation, *Catal Lett*, 50 (1998) 205-209.
- [16] T. Masui, Y. Peng, K.-I. Machida, G.-Y. Adachi, Reduction Behavior of CeO₂-ZrO₂ Solid Solution Prepared from Cerium Zirconyl Oxalate, *Chem Mater*, 10 (1998) 4005-4009.