Research progress on low-concentration methane oxidation using palladium-based catalysts

Zhehua Du

Wuhan Second Ship Design and Research Institute, Wuhan, Hubei, 430205, China

Abstract. There is low concentration (0.05% to 0.5%) of CH4 leakage in marine natural gas engine exhaust. It is difficult to capture and utilize low concentration CH4 because of its stable chemical structure and high ignition temperature. Catalytic oxidation is the main method to remove low concentration CH4 from tail gas. The noble metal palladium (Pd) is the best catalytic material for the complete oxidation of low concentration CH4. In this paper, the main research progress of Pd-based catalysts is reviewed for their low-temperature activity, reliability and development cost. Initially, the impact of Pd particle dimensions and valence distribution, Pd dispersion, carrier identity and strong metal-carrier interaction (SMSI) on the catalyst's methane oxidation activity was elucidated. Then, the mechanism of methane oxidation on the surface of Pd-based catalysts is summarized; In addition, the deactivation mechanisms of Pd-based catalysts, such as high temperature sintering, water poisoning and sulphur poisoning, are described in detail. In conclusion, the major hurdles encountered in achieving full oxidation of methane at low concentrations are outlined, along with the future development direction for methane oxidation catalysts. Additionally, strategies to enhance the performance of Pd-based catalysts are briefly suggested. The modified Text maintains a clear, professional, and concise style with minimal changes.

1. Introduction

International shipping greenhouse gas emission control is an important part of global greenhouse gas emission reduction, and is also a common responsibility and challenge faced by the global shipping industry. Compared with conventional fuel power, the use of liquefied natural gas (LNG) can achieve an immediate carbon reduction of more than 20% over the entire industry chain cycle, while reducing more than 85% of NO_x emissions and 99% of SO_x emissions. The escape of unburned CH_4 (about 0.05%-0.5% concentration) caused by insufficient combustion in the cylinder of natural gas engines has become one of the most important sources.

2. Low concentration methane catalytic oxidation technology

The core of catalytic oxidation technology is to obtain a highly active and reliable catalyst for the target reaction. The following technical challenges are usually faced.

- Problem of catalyst activity at low temperature.
- Problem of catalyst reliability under harsh working conditions.
- Problem of expensive catalyst development.

Corresponding author's e-mail: shunli878@163.com

Ford developed Pd/Rh catalyst for the first time in 1989. Compared with other precious metal catalysts, PD-based catalysts not only have high economy, excellent heat resistance and sintering property, but also have better oxidation efficiency for hydrocarbons [1]. Research on PD-based catalysts focuses on solving such problems as low temperature ignition of CH_4, inhibition inactivation of H_2O, CO or SO_x poisoning, high temperature stability and durability, and cost [2].

3. Study on structure-activity relationship of Palladium-based catalyst

3.1 Effect of Pd particle size distribution

The change of Pd particle size will affect exposed crystal surfaces and unsaturated sites. Moreover, the bond energy between Pd and O is changed, which reflects the structural sensitivity. Hicks [3] first explored the influence of Pd particle size on the catalytic oxidation process of catalyst. Studies have shown that compared with the catalyst, the unit activity check point turnover frequency (TOF) of Pd particles with 4.0mm particle size is higher, and the apparent activation energy is almost the same. Stakheev [4] found that when Pd particle size increased from 1nm to 20nm under lean combustion conditions, TOF of the catalyst increased linearly. This further confirmed the structural sensitivity of methane oxidation in terms of Pd particle size under oxygen-enriched conditions. PdO particles with large particle size has better catalytic performance.

3.2 Effects of Pd dispersion and valence distribution

The dispersion state and valence state distribution on the surface are related to reaction activity. Huang [5] prepared La-Al_2O_3 catalyst modified by Ce-Zr by the initial wet impregnation method. It was found that Pd and PDO can be used as active check point of CH_4 oxidation, while PDO only plays a leading role under rich combustion conditions. Murata [6] pointed out that the core-shell structure formed Pd@PDo metal oxide support has the best activation effect on CH_4.

3.3 Effect of carrier on catalytic activity

The properties of carrier also affect the oxidation process of CH_4. Studies by Yoshida [7] show that Pd species are more reactive than Pd species on strong acids and basic oxides, as shown in Figure 1.

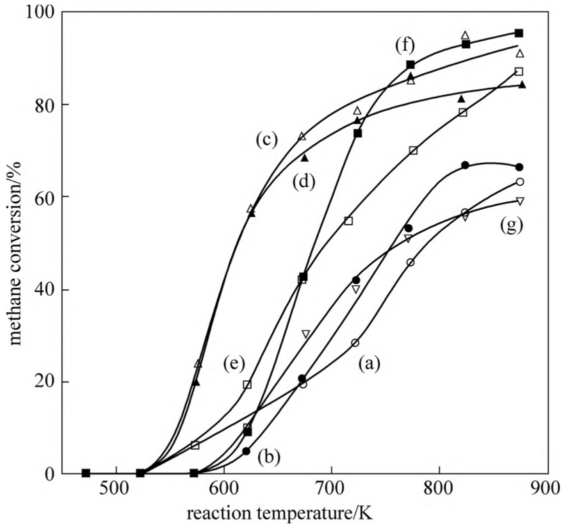

Figure 1. Methane conversion over Pd-based catalysts with different supports

The exposed crystal surface of carrier also affects the oxidation performance of CH_4. Chen [8] synthesized CeO_2 carriers with nano-rod-like, cube and octahedral morphology and further loaded Pd. The result is shown in Figure 2.

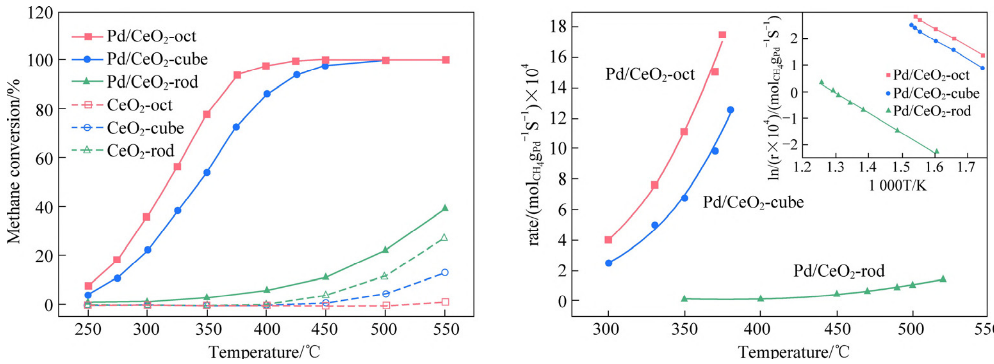

Figure 2. CH_4 conversion and reaction rate with different CeO_2 supports

3.4 Effect of strong metal-support interaction

SMSI is the focus of catalyst design. SMSI usually involves such processes as charge transfer between surface interface, species overflow, carrier coating of metals, and component morphological changes, as shown in FIG. 3 [9].

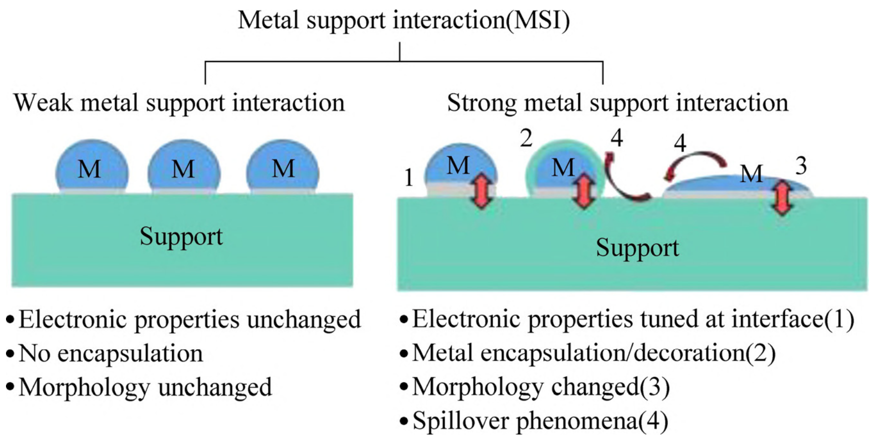

Figure 3. Comparison between WMSI and SMSI

4. Study on Methane Oxidation Mechanism of Pd-based Catalyst

Eley-Rideal and Langmuir-Hinshelwoo models are the earliest known mechanisms for CH_4 oxidation of PD-based catalyst. Pd species on the catalyst surface first adsorbed CH_4 and O_2 at the active check point following Langmuir-Hinshelwoo mechanism, and then catalyzed the oxidation of CH_4 [10], which is also a generally accepted reaction process at present. The mechanism is shown in Figure 4.

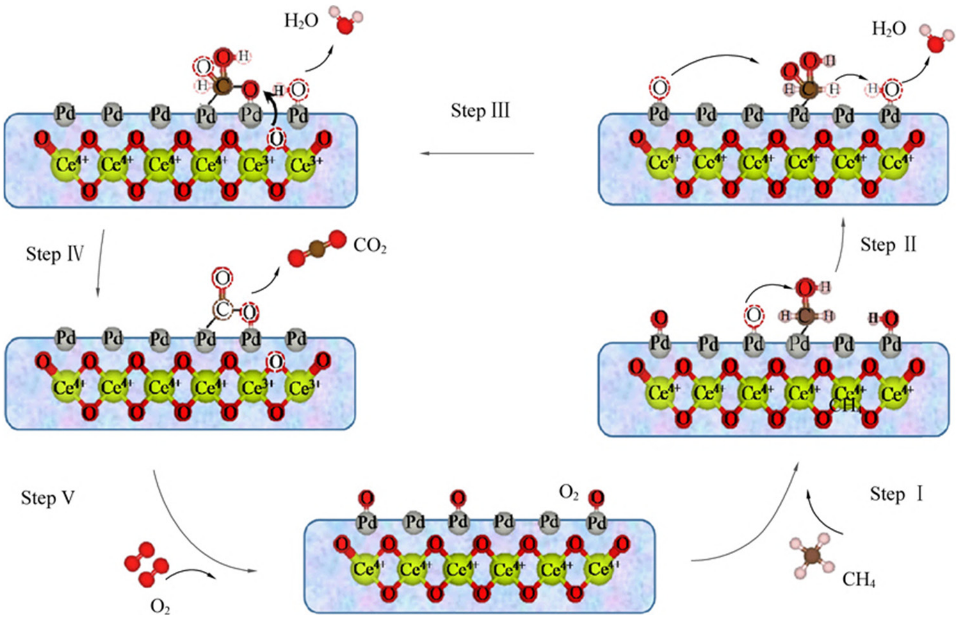

Figure 4. Methane oxidation on the Pd-Ce-Zr catalyst

5. Study on deactivation mechanism of PD-based catalyst

5.1 Mechanism of high temperature deactivation

Although using SMSI effect between Pd and CeO_2 can effectively inhibit the sintering agglomeration of Pd species, SMSI effect may also initiate the deactivation of the catalyst. The mode of deactivation associated with SMSI effect may be electronic effect [10]. The mechanism is shown in Figure 5.

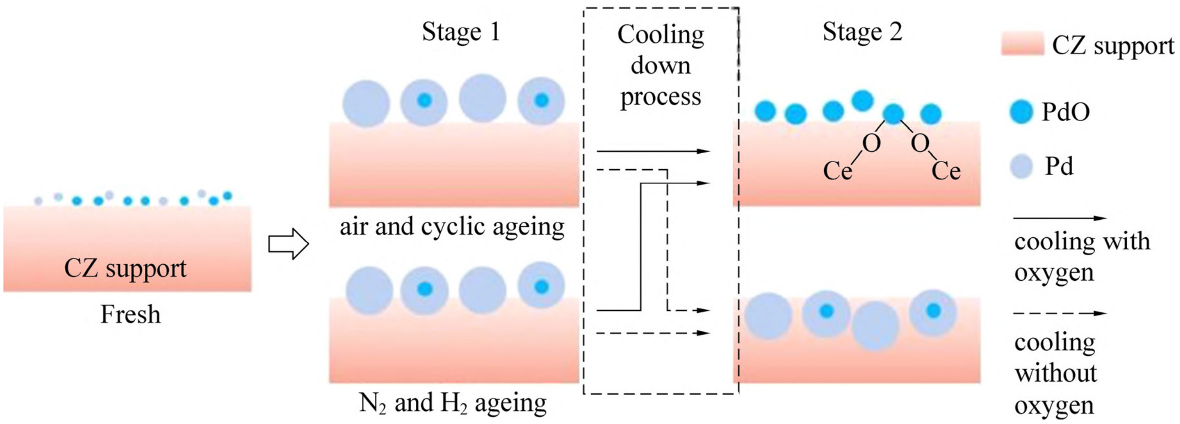

Figure 5. Pd species modified $Ce_{0.5}Zr_{0.5}O_2$ surface to enhance anti-aging properties of catalysts

5.2 Mechanism of water intoxication

Cullis [7] proposed that surface hydroxyl groups may inhibit active check point. Another study by Ciuparu [7] found that accumulation of surface $Pd(OH)_2$ would interfere with the migration process of surface reactive oxygen species, as shown in Figure 6.

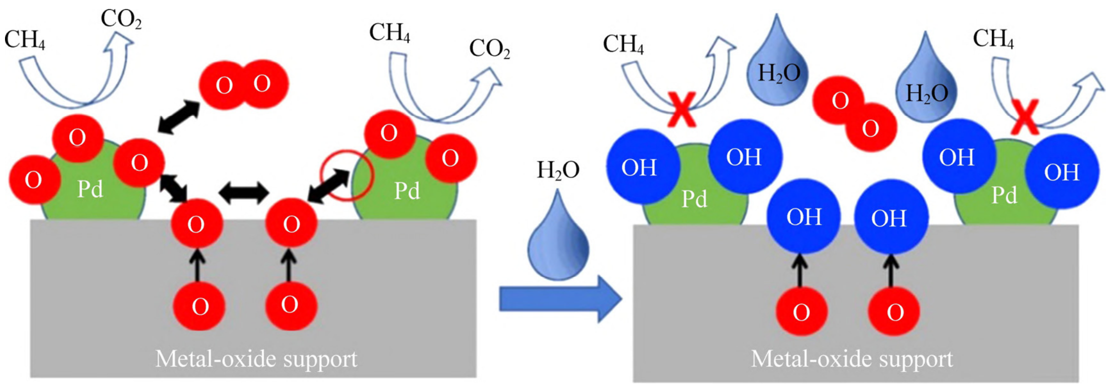

Figure 6. H_2O poisoning deactivation Pd-based catalyst

5.3 Mechanism of sulfur poisoning

Catalysts can be poisoned and deactivated by long-term exposure to sulfur-containing exhaust gases. It has been confirmed that SO_x in the exhaust gas can lead to the sulfurization of catalyst support or active components under the condition of dilute combustion above 200℃ [6], as shown in Figure 7.

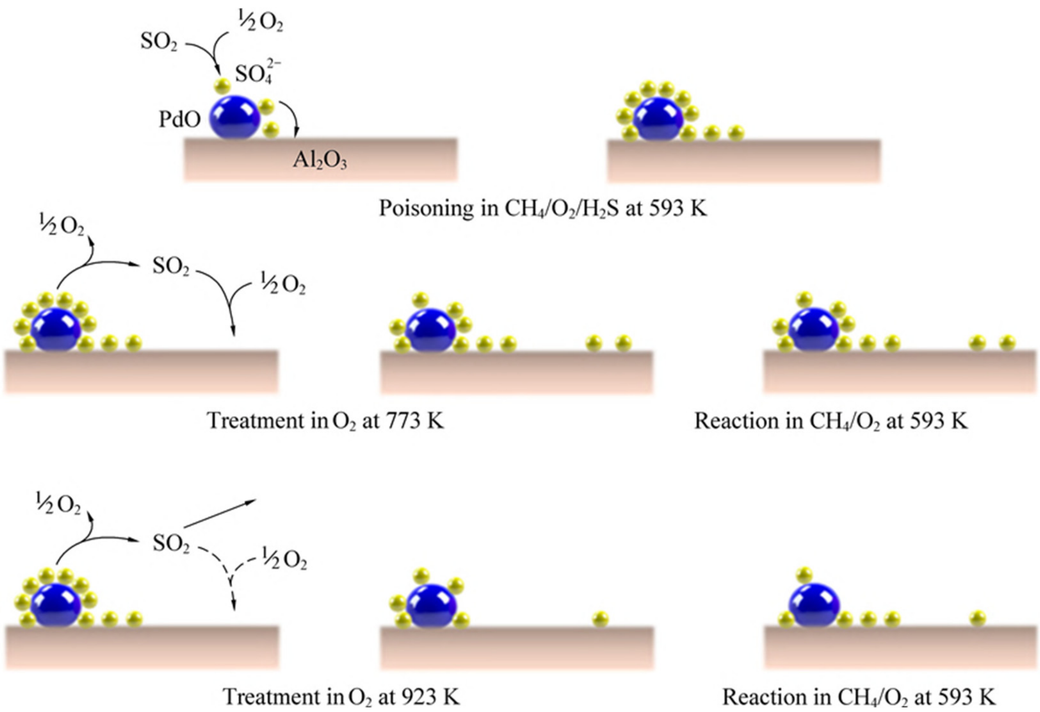

Figure 7. Spoisoning and regeneration mechanisms

6. Conclusion

Pd-based metal oxides is the most widely used catalyst for CH_4 oxidation. Low-cost design and development of more catalysts with low temperature and high efficiency, excellent water resistance and sulfur resistance, and high durability are the key research and development directions in the future. Therefore, it is necessary to continue to design the catalyst structure at the molecular level.

References

1. Cargnello M. (2012) Exceptional activity for methane combustion over modular Pd@CeO_2 subunits on functionalized AlO_3. Science,337 (6095): 713-717.
2. Xiong H. (2018) Design considerations for low-temperature hydrocarbon oxidation reactions on Pd based catalysts. Applied Catalysis B: Environmental, 236:436-444.
3. Ciuparu D. (2002) Catalytic combustion of methane over palladium-based catalysts. Catalysis Reviews, 44 (4): 593-649.
4. Robert F. (1990) Structure sensitivity of methane oxidation over platinum and platinum palladium. Journal of Catalysis,122:280-294.
5. Stakheev A.Y. (2013) Particle size effect on CH_4 oxidation over noble metals: Comparison of Pt and Pd catalysts. Topics in Catalysis,56 (1-8):306-310.
6]. Yoshida H. (2007) Support effect on methane combustion over palladium catalysts. Applied Catalysis B: Environmental, 71 (1-2): 70-79.

https://doi.org/10.1051/e3sconf/202338504033

7. Chen S. (2021) Elucidation of active sites for them CH_4 catalytic oxidation over Pd/CeO_2 via tailoring metal-support interactions. ACS Catalysis, 11 (9): 5666-5677.
8. Cao Y. (2023) Progress on metal-support interactions in Pd-based catalysts for automobile emission control. Journal of Environmental Sciences, 125:401-426.
9. Li K. (2018) The Electric field promoted ultra-lean methane oxidation over Pd-Ce-Zr catalysts at low temperature. Molecular Catalysis, 459:78-88.
10. Dragos Ciuparu L.P. (2001) Support and water effects on palladium based methane combustion catalysts. Applied Catalysis A: General,209:415-428.