



Review Methane Combustion over Zeolite-Supported Palladium-Based Catalysts

Jinxiong Tao, Yuxi Liu, Jiguang Deng, Lin Jing, Zhiquan Hou, Lu Wei, Zhiwei Wang and Hongxing Dai *🕩

Beijing Key Laboratory for Green Catalysis and Separation, Key Laboratory of Beijing on Regional Air Pollution Control, Key Laboratory of Advanced Functional Materials, Education Ministry of China, Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemical Engineering, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, China

* Correspondence: hxdai@bjut.edu.cn; Tel.: +86-10-6739-6118; Fax: +86-10-6739-1983

Abstract: The emission of methane leads to the increase in the methane concentration in the atmosphere, which not only wastes resources but also intensifies the greenhouse effect and brings about serious environmental problems. Catalytic combustion can completely convert methane into carbon dioxide and water at low temperatures. However, the catalytic activities of the conventional supported palladium catalysts (e.g., Pd/Al_2O_3 and Pd/ZrO_2) are easy to decrease or the two catalysts can even be deactivated under actual harsh reaction conditions (high temperatures, steam- and sulfur dioxide-containing atmospheres, etc.). Recently, noble metal catalysts supported on zeolites with ordered pores and good thermal stability have attracted much attention. This review article summarizes the recent progress on the development and characteristics of zeolite-supported noble metal catalysts for the combustion of methane. The effects of framework structures, silica/alumina ratios, acidity, doping of alkali metals or transition metals, particle sizes and distributions, and their locations of/in the zeolites on methane combustion activity are discussed. The importance of developing high-performance catalysts under realistic operation conditions is highlighted. In addition, the related research work on catalytic methane combustion in the future is also envisioned.

Keywords: methane combustion; zeolite; supported noble metal catalyst; palladium-based catalyst; catalytic oxidation mechanism

1. Introduction

As an attractive energy source, methane is more economical and friendly to the atmosphere than the other fossil fuels, and furthermore, methane possesses a high energy density with a high H/C ratio. Natural gas (its main component is methane) can be used as a fuel in compressed natural gas (CNG) vehicles, and its combustion in CNG vehicles leads to lower emissions of CO₂, CO, non-CH₄ hydrocarbons, and NOx than that in traditional diesel or gasoline vehicles. It has been reported that the above emissions could be significantly reduced if the energy source was replaced by natural gas [1,2]. With a higher fuel combustion efficiency, lean-burn natural gas vehicles (NGVs) emit up to 21% less greenhouse gas than their gasoline or diesel counterparts. Complete oxidation of methane to CO₂ can effectively reduce its environmental impact by more than 96% as compared with the direct emission of methane to the atmosphere. Up to now, it has been well-recognized that CH₄ plays an indispensable role in the paradigm shift to a more sustainable planet. However, natural gas engines still emit significant amounts of unburnt CH₄ (so-called methane slip) in stationary applications (power plants). The lifetime of CH_4 in the atmosphere is much shorter than CO_2 , but CH_4 is more efficient than CO_2 in trapping radiation. In the past 100 years, the global warming potential of CH_4 has been reported to be 28–36 times higher than that of CO_2 [3–5].

Catalytic combustion of CH_4 provides an alternative pathway to its thermal combustion. Under the fuel-lean conditions, due to the overheating of methane combustion,



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). more nitrogen oxides are produced. In this review article, we put the emphasis on the combustion of methane emitted from stationary and mobile sources. Due to the high temperatures generated during the methane combustion process under the fuel-lean conditions, more nitrogen oxides are produced. For the combustion of low-concentration methane, the emergence of adsorption enrichment technology provides another pathway for the comprehensive utilization of lean methane. Membrane separation and pressure swing adsorption technologies are mainly used in practice, which can enrich the methane concentration. However, it is not widely used in industry because the costs of operation and preparation exceed the economic benefit of increasing the concentration. An ideal catalyst design should take into consideration the low-temperature operation and long-term stability [6]. The low operation temperature is important in minimizing the generation of the secondary pollutants emissions (e.g., NO_x) in CH₄ combustion or making the system achieve low CH₄ emission standards for the removal of CH₄.

Up to now, there have been a large number of catalysts (transition metal oxides, mixed metal oxides (e.g., ABO₃, A₂BO₄, and A₂B₂O₇), (conventional supports or zeolites)supported noble metals, and hexaaluminates (MAl₁₂O₁₉)) developed in the literature. The noble metal-based catalysts used in methane combustion are mainly Pd, Pt, Rh, and Au. Generally speaking, their activity sequence is Pd > Pt > Rh > Au. Among them, Rh is expensive and easy to volatilize and lose at high temperatures, while Au has the worst activity for methane combustion and is generally used as a cocatalyst, such as Pd-Au, Pt-Au, etc. Pd shows the highest activity and light-off activity at low temperatures, and it is not volatile at high temperatures. Moreover, Pd-based catalysts exhibit better catalytic performance for the combustion of alkanes (C_{3+}) . In addition, some non-Pd-based catalysts are discussed in Section 2.5. Compared with the other noble metal catalysts, supported Pd catalysts are the most widely and deeply studied. Although the microscopic mechanism is still unclear, we can get a glimpse of catalytic methane combustion with the development of more advanced characterization methods and theoretical computational chemistry. Therefore, we summarize the main research progress of Pd-based catalysts in this review article. Up to now, various catalysts have been developed to promote CH_4 combustion, including platinum group metals (PGM), transition metal (no-PGM) oxides, perovskite-type or -like oxides, and hexaaluminates [7–13]. To date, there have been some review articles on catalytic CH_4 combustion in the literature [3,7,14], which summarized the catalyst choice and their properties, support effects, active center nature, reaction kinetics, water resistance, and sulfur dioxide-poisoning mechanism, as well as the impact of the operating conditions. Among all the reported catalysts, platinum group catalysts show the highest intrinsic activities at low temperatures and can achieve a nearly 100% CH₄ conversion below 600 °C. However, the reaction rates of transition metal oxide catalysts are generally lower by 3–5 orders of magnitude, and methane conversion can reach 100% only at an operating temperature above 600 °C.

In the past decades, there has been a tremendous interest in developing highperformance low-temperature CH₄ oxidation catalysts [15,16], and the Al₂O₃-supported Pd-based materials remain one of the highly efficient catalysts. Of course, Pt- and Rh-based catalysts are also considered to be excellent candidates for catalytic methane combustion. Although Pt is typically doped in commercial catalysts to improve the thermal stability and sulfur dioxide resistance, Pd is the major catalytic active site. The big challenge is that H₂O (typical concentration = 5–15 vol%) and SO₂ (typical concentration = 1–30 ppm) in the exhaust gas results in severe deactivation of the catalysts that decrease the CH₄ removal efficiency. Many available supports have been reported, such as Al₂O₃ [17–23], CeO₂ [24–27], Ce_{1-x}Zr_xO₂ solid solutions [28–30], and SnO₂ [31–34]. Zeolites with various additives have also been used in methane combustion. Each type of support possesses some beneficial features. For instance, Al₂O₃ has a relatively low cost and a large specific surface area. CeO₂- and Ce_{1-x}Zr_xO₂-supported catalysts exhibit a large oxygen storage release capacity due to the presence of the Ce⁴⁺/Ce³⁺ redox couple, while doping Zr into the lattice of CeO₂ to form a Ce-Zr solid solution can strongly improve the thermal stability of the catalyst. Zeolite-supported catalysts demonstrate better water tolerance than other compounds-supported catalysts. Of course, each of these catalysts possesses some obvious advantages and disadvantages. The noble metal components are generally supported on various metal oxides (e.g., Al₂O₃, CeO₂, ZrO₂, Co₃O₄, and SiO₂) for lean methane combustion. For example, the Pd/CeO_2 and $Pd/Ce_xZr_{1-x}O_2$ catalysts exhibited a better performance at low temperatures than other supported noble metal catalysts due to the support of CeO₂ or $CexZr_{1-x}O_2$ possessing the Ce^{4+}/Ce^{3+} redox couple that could indirectly affect the performance of the catalyst, while doping Zr to the lattice of CeO_2 to generate a Ce-Zr-O solid solution could strongly improve the thermal stability of the catalyst [28,29]. Willis et al. [35] used SiO₂ (inert), Al₂O₃ (acidic), $Ce_{0.8}Zr_{0.2}O_2$ (redox), and MgO (alkaline) as support materials and found that, although the above oxide-supported Pd catalysts possessed similar activation energies for methane combustion, the activity of the MgO-supported Pd catalyst was obviously low. The authors believed that basic MgO enhanced the stability of the electron-rich PdO phase, which led to the increase in energy required to form oxygen vacancies and the decrease in the methane reaction rate. In addition, MgO could easily adsorb CO₂ to generate magnesium carbonate, which covered the active sites, influencing the surface of the Pd particles or the interface between the Pd and the carrier, and hence giving rise to a decreased catalytic activity.

It is well-known that low-temperature CH₄ oxidation over Pd-based catalysts follows a Mars—van Krevelen (MvK) redox mechanism. Garbowski et al. investigated the physicochemical properties of the Pd/ γ -Al₂O₃ catalyst by combining nano-diffraction, electron microscopy, and Fourier transform IR (FT-IR) analysis [36]. The authors proved that the MvK reaction mechanism was suitable for explaining the kinetic behavior of CH₄ oxidation. Over the supported noble metal (e.g., Pd and Pt) catalysts, CH₄ is first adsorbed on the surface of the active nanoparticles (NPs) and dissociated into the adsorbed methyl species. Because methane has a highly symmetrical tetrahedral structure with a C–H binding energy of 435 kJ/mol, the first step of bond breaking is the rate-limiting step [37]. Under the action of oxygen, intermediate species (such as HCHO and carbonate) are generated and finally converted to CO_2 and H_2O as products. The catalytic activity of methane oxidation is controlled by different oxygen species, among which lattice oxygen (Olatt) and surface oxygen (Osur) are the main oxygen species. In the low-temperature stage of CH4 oxidation, the increase in the amount of the O_{sur} species can greatly enhance the catalytic activity of the catalyst, while in the high-temperature stage of CH_4 oxidation, the increase in the amount of the O_{latt} species can greatly improve the catalytic activity of the catalyst. In this process, the adsorption and desorption between CH₄ and CH₄^{*} are very fast processes, and at the same time, the gas-phase oxygen in this process combines with the catalyst to generate a series of O_{sur} and O_{latt} species, so the rapid transformation of CH₄^{*} and [O] is a critical factor in the catalytic combustion of low-concentration CH₄.

As pointed out above, Pd-based catalysts are thought to be the most active for combustion of CH_4 under lean conditions. It is known that the activity of the Pd/Al_2O_3 catalyst is seriously inhibited by water vapor and its gradual deactivation takes place. Promotion brought about by suitable supports has been reported. A support is important for enhancing the catalytic activity and stability of a supported noble metal catalyst. In comparison to γ -Al₂O₃, α - and θ -Al₂O₃ could offer weaker Pd-Al₂O₃ interactions that helped to expose more Pd step sites [38]. Upon increasing the calcination temperature, the crystalline structure of ZrO_2 was transformed from the mixed phase (monoclinic and tetragonal) to the pure tetragonal phase, and the tetragonal ZrO₂-supported Pd catalysts exhibited good hydrothermal stability [39]. Moreover, doping part of the Zr to the lattice of CeO_2 to form a $Ce_{1-x}Zr_xO_2$ solid solution can greatly improve the thermal stability of the $Ce_{1-x}Zr_xO_2$ -supported noble metal catalyst. Although such a deactivation is reversible to some extent, it affects the normal working status of the catalyst in a specific environment. Schwartz et al. thought that H_2O poisoning of the supported Pd catalyst was caused by the adsorbed OH species, which covered the catalyst surface to form the stable and inactive $Pd(OH)_2$ phase [40]. However, the intrinsic CH₄ combustion activity of Pd/SiO₂ is

much lower than that of Pd/Al_2O_3 . Different from Pd/SiO_2 , Pd/Al_2O_3 experienced severe low-temperature steam poisoning when it was exposed to an excessive steam atmosphere. As a unique class of microporous and crystalline solids, aluminosilicate zeolites have hence been considered to be one possible selection for decreasing the negative effect of water on CH₄ combustion. Aluminum oxide and zirconium oxide are usually used as supports for loading the noble metals in methane combustion. In addition to aluminum oxide and zirconium oxide, zeolites are also a kind of important support used for loading the noble metals. Hence, we put the emphasis on the zeolites used for loading the noble metals in methane combustion.

Zeolites are an attractive class of shape-selective materials with regular microporous aluminosilicates, controlled acidity, and good (hydro)thermal stability. Such microporous materials have been used in adsorption and separation, petroleum refining, energy and chemical industries, environmental protection, and other fields because of their structural characteristics (pore structures and pore sizes), specific adsorption performance of small molecules, and high specific surface areas [41]. The framework illustrations of the support types of the main zeolites and some mesoporous silicas were used for the complete combustion of methane in this review, as shown in Table 1 and Figure 1. Zeolites are also effective catalytic materials, although they cannot catalyze methane combustion independently. For this reason, zeolites are often used as supports for dispersing metal NPs to increase functionality. Complex strategies are also developed to prepare composite zeolites with core-shell structures. Specifically, the design and development of zeolite-supported metal catalysts (e.g., precious metals) and NPs doped in zeolites have strengthened the application of zeolites in CH₄ activation. We may ignore that there seems to be no correlation between the dimensions/pore diameters of zeolite supports. Therefore, other characteristics of zeolites that improve catalytic activity and stability deserve further study.

Table 1. Structural properties of zeolites with different topologies and mesoporous silicas.

Framework Type	Material Name	Dimensionality	Ring Type (Pore Type)	Limiting Pore Size (nm)
CHA	SSZ-13	3D	8/6/4 (micropore)	0.38 imes 0.38
LTA	LTA	3D	8/6/4 (micropore)	0.41 imes 0.41
MFI	ZSM-5	3D	10/6/5/4 (micropore)	0.53 imes 0.56
BEA	Beta	3D	12/6/5/4 (micropore)	0.66 imes 0.67
FAU	Χ, Υ	3D	12/6/4 (micropore)	0.33 imes 0.33
SBA-15	-	1D	-/-/- (mesopore)	4.6-10.0 [42]
MCM-41	-	1D	-/-/- (mesopore)	10.0 [43]
KIT-6	-	3D	-/-/ (mesopore)	4.0–12.0 [44]

Note: The information for the microporous zeolites is obtained from the "Database of zeolite structures" by the Structure Commission of the International Zeolite Association (IZA-SC), whereas the information for the mesoporous zeolites is cited from the references as noted.

This review article summarizes the recent literature progress of zeolite-supported Pd catalysts for the complete oxidation of methane in an excess supply of oxygen, which includes both methane combustion and lean exhaust methane emission control, and discusses the relationship between various physicochemical properties (including zeolite framework architectures, silica/alumina ratios, acid sites, and noble metals particle sizes and their dispersion) and the catalytic performance or stability of the zeolite-based noble metal catalysts. The design and development of zeolite-supported precious metals catalysts and precious metals NPs doped in zeolites are also strengthened for the application of zeolites in CH_4 activation. A brief summarization of most of the publications that reported complete combustion of methane is presented in Table 2 for comparison purposes, and the discussion will focus on fundamental issues regarding the nature of the active sites and associated anchoring sites in zeolite supports. The stability of the zeolite-supported catalysts in the high-concentration water vapor or SO_2 atmospheres and their deactivation due to sintering are also investigated. Finally, the challenges and prospects of such a topic in the future work are presented.



Figure 1. Framework images of (a) CHA, (b) FAU, (c) LTA, (d) MFI, and (e) BEA (obtained from the IZA-SC).

2. Zeolite Types Used in Catalytic Methane Combustion

2.1. Small-Pore Zeolites with 8 Member Rings

SSZ-13 is a typical CHA-structured molecular sieve with small pores and eight member rings, which has a large specific surface area and an abundant acid amount. Zeolites with eight member rings have a high potential to inhibit the aggregation of metal cations under reaction conditions due to their small pore sizes (0.38 nm \times 0.38 nm) and good hydrothermal stability compared with the medium- and large-pore zeolites. Recently, Cui et al. have reported that when the Pd loading in Pd/SZZ-13 was increased to 2 wt% or more, the sizes of the PdO particles were 2.5 \pm 1.5 nm; the decrease in the CH4 oxidation rate with the drop in Pd content was attributed to the generation of a greater amount of the isolated Pd(II) ions that were less active than the PdO NPs formed at higher Pd contents [45]. These findings are in good agreement with those previously reported by Friberg et al. [46]. However, the hydrothermal aging of SSZ-13 at high temperatures (>850 °C) can cause structural destruction, giving rise to a decreased surface area, pore volume, and change in the XRD pattern [47]. Friberg et al. studied the effect of Pd loading on CH₄ oxidation of the thermally stable LTA zeolite with a Si/Al ratio of 44 and after hydrothermal aging at temperatures as high as 900 °C [48]. After hydrothermal aging at temperatures of \leq 700 °C, the Pd/LTA exhibited a high and stable CH₄ combustion performance in the presence of water vapor. These authors found that the deactivation of the catalyst was not caused by the structural collapse of the LTA zeolite, and the $T_{50\%}$ over the Pd/LTA was 41 $^{\circ}$ C lower than that over the Pd/Al₂O₃. After thermal aging at 700 $^{\circ}$ C, the difference in the $T_{50\%}$ was 20 $^{\circ}$ C. Thermal aging at higher temperatures (800 and 900 °C) resulted in a higher $T_{50\%}$ (68 and 118 °C) over the Pd/LTA, respectively.

2.2. Medium-Pore Zeolites with 10 Member Rings

ZSM-5 was first synthesized in 1972 using the hydrothermal method with quaternary ammonium salts as the template agent [49]. The pore size of ZSM-5 is 0.55 nm \times 0.51 nm, and this material shows a 10-element ring pore with a linear shape parallel to the *b*-axis direction and an elliptical pore with a pore size of 0.53 nm \times 0.56 nm. As early as 1994, Li and Armor loaded Pd on ZSM-5 through the ion exchange approach and found that Pd/ZSM-5 exhibited excellent low-temperature methane combustion activity [50]. The higher catalytic activity of the Pd-based zeolite catalyst has been thought to be related to the additional lattice oxygen that can readily activate methane at low temperatures. All the zeolite catalysts reported in these early studies were prepared by the ion exchange

method. Liu et al. pointed out that the glow discharge plasma treatment of the Pd-loaded zeolite catalysts before calcination could reduce the light-off temperature and improve the stability of the catalysts [51]. Hosseiniamoli et al. evaluated the stability of Pd/TS-1 and Pd/Silicalite-1 at 400 °C and a relative humidity (RH) of about 80% [52]. It was found that Pd/Silicalite-1 gradually became inactive after 30 h of operation, but the activity of Pd/TS-1 remained stable after 1900 h of reaction. The extended X-ray absorption fine structure (EXAFS) analysis of the Ti *K*-edge and Pd *K*-edge proved the anchoring effect of Ti on Pd, and the high stability of the porous catalyst was mainly assigned to the hydrophobicity and low acidity of the aluminum-free molecular sieve. Rational use of newly developed techniques could improve the dispersion of PdO and enhance its interaction with the zeolite support.

High-Si zeolites with an MFI framework have recently gained much attention, probably due to the water-related problems and the increasing interest in its hydrophobic property. For example, silicalite-1 (S-1) is an Al-free MFI zeolite and thus lacks acidic sites, but it is highly hydrophobic and hydrothermally stable. Wang et al. claimed that the Pd particles confined in S-1 and the synthesized core-shell catalysts showed high activities at low temperatures, with a shielding impact on H₂O resistance [53]. Furthermore, due to the hydrophobicity of S-1, Pd@S-1 was able to selectively prevent water vapor from diffusing into the Pd sites, exhibiting outstanding water resistance. In addition, Pd@S-1 and Pd_{0.8}Ni_{0.2}@S-1 showed the $T_{90\%}$ of 385 and 412 °C in the presence of 5 vol% water vapor [54], respectively. It is widely accepted in a number of the literature works that the small PdO NPs encapsulated in the zeolitic crystals are the active sites, which can prevent Pd from migrating and sintering and improve the stability of the zeolite-supported PdO catalysts under harsh conditions.

2.3. Large-Pore Zeolites with 12 Member Rings

In addition to the small and medium pore size zeolites mentioned above, the noble metal catalysts supported on large pore size zeolites (BEA, pore size = 0.7-0.8 nm) for CH₄ combustion applications have also been reported before. For example, Zhang et al. deposited Pd on the dealuminated zeolite support via a reduction-deposition route to generate the high-efficiency Pd/beta catalyst for lean CH_4 combustion [55]. The Pd/beta catalyst at a Pd loading of 0.5 wt% showed excellent catalytic activity (methane conversion > 99% at 375 °C) and good stability. The good performance of Pd/beta was ascribed to the highly dispersed PdO NPs, abundant adsorbed oxygen species, stable PdO, rich Pd^{n+} (0 < n < 2) species anchored at the T-atom site, and enhanced hydrophobicity. It is generally recognized that dealumination can reduce the crystallinity of a zeolite and lead to the formation of the aluminum species outside the acidic framework, which further promotes the sintering of palladium particles. Subsequently, they also introduced an organic ligand of 3-mercaptopropyl trimethoxysilane (MPTS) to stabilize the Pd precursor during the preparation process, which was used to confine the PdO NPs in the beta zeolite [56]. The asobtained sample demonstrated prominent CH₄ combustion activity (99% CH₄ conversion at 360 °C) and exhibited a remarkably better anti-sintering property and long-term (50 h) stability than the Pd/beta-IW and Pd/beta-HT samples. Kröcher et al. designed a porous catalyst based on Pd and a hierarchical zeolite with the fully Na-exchanged acid sites, which improved the support stability and prevents steam-induced Pd sintering under the reaction conditions by confining the noble metal within the zeolite [57]. Under the dry and wet conditions, the $T_{50\%}$ values over Pd/Na-MOR were 340 and 375 °C, respectively. There was no deactivation of this catalyst after 90 h of reaction in the presence of water. Ghorbel et al. prepared the Pd and Pd-Mo catalysts supported on HY and NaY and studied the effect of molybdenum doping on the activity of the catalyst [58]. It was found that Pd/HY and PdMo/NaY were less active than Pd/NaY at 500 °C. The catalytic activity of the monometallic sample increased with the reaction time, whereas that of the bimetallic sample decreased. The comparison of the catalytic activity of Pd/HY or PdMo/NaY

revealed that the basicity of the support enhanced the oxidation ability of Pd by a rise in the electronic density of the metal particles on the sample surface.

2.4. Mesoporous Zeolite and Mesoporous Silicas Catalysts

The pore sizes of the conventional zeolites are generally less than 2 nm, and the reactants can be readily blocked from entering the active centers. The introduction of another set of mesopore nanochannels (so-called mesoporous zeolites) can considerably enhance the mass transfer efficiency, which structurally favors most of the reactions. Mesoporous silica zeolites are one of the most attractive catalytic materials for methane combustion because of their good chemical stability at high temperatures. More importantly, the mesoporous channels of such materials can provide limited space for the formation of Pd NPs with suitable sizes, and control the Pd species in their most active state, which shows the interesting activities of the as-designed catalysts [59].

Hussain et al. prepared the mesoporous silica-supported Pd catalysts and measured their catalytic activities for methane combustion [60]. Benefiting from the suitable structure and pore size of the silica, all the as-obtained Pd catalysts exhibited an almost complete conversion of CH₄, although the catalysts with the lowest Pd loading showed a methane conversion of 90% at 650 °C, whereas the maximum Pd loading in the KIT-6-supported catalyst allowed for a decrease in the temperature ($T_{90\%}$ = 405 °C for complete conversion of nethane). Yuranov and coworkers successfully encapsulated Pd NPs with particle sizes of 1.0–3.6 nm within the channels of SBA-15 using the ion exchange strategy [61]. It was found that through the ion exchange of the surface silanol groups with [Pd(NH₃)₄]²⁺, the Pd loadings (0.1–4.4 wt%) could be further increased. The transmission electron microscopic (TEM) investigations of 2.1 wt% Pd/SBA-15-extr. indicated that most of the Pd NPs were located inside the mesoporous channels. The 2.1 wt% Pd/SBA-15 catalyst showed a stable catalytic activity in 6 h on-stream methane combustion at 520 °C.

The above research advances exemplify the feasibility of mesoporous silica (especially SBA-15) as a support for loading Pd and the effectiveness of the ion exchange method in maximizing the reactivity of the Pd species in methane combustion. Murthy et al. used the sol immobilization (SI) method instead of the conventional initial wet impregnation (IWI) method to prepare uniform Pd NPs confined in ordered mesoporous SBA-15 and determined their activities for methane combustion [62]. Compared with the catalyst derived from the conventional IWI method, the one derived from the SI route possessed uniform Pd NPs with a size of 5 nm in the channels of SBA-15 and still maintained such a size even after thermal aging in air at 800 °C for 3 days. The thermally stable Pd/SBA-15-SI catalyst showed excellent activity for CH₄ combustion ($T_{50\%} = 300$ °C and $T_{90\%} = 350$ °C), which was consistent with the result reported in the literature [63]. Afterward, Zribi et al. also synthesized a highly dispersed PdO (particle size = 2 nm) phase in MCM-41, and the Pd(II) complex with a monoamine ligand was used to prevent precipitation of the Pd (Pd Pd Pd).

The doping of a substance with a redox nature is conducive to the construction of the metal—support interaction, improves stability of the target catalyst, and reduces the use of precious metals [10,19,21]. Liotta et al. prepared the SBA-15-supported LaMn_{0.4}Fe_{0.6}O₃ catalysts with perovskite loadings of 10, 30, and 40 wt% and found that the CH₄ combustion activity of the Pd/30 wt% LaMn_{0.4}Fe_{0.6}O₃ /SBA-15 catalyst was improved compared with that of the Pd/LaMn_{0.4}Fe_{0.6}O₃ catalyst [65]. The Pd/30 wt% LaMn_{0.4}Fe_{0.6}O₃ /SBA-15 catalyst also showed excellent SO₂ tolerance. Based on the structure and spectral characterization results, the optimized catalytic activity was due to the high dispersion of the active sites and good resistance to sintering during the reaction process. Yin et al. used the impregnation method to prepare a series of catalysts with different Pd loadings and investigated their catalytic activities and stability under the lean CH₄ combustion conditions [66]. The introduction of ZrO₂ as a promoter led to the enhancements in the oxygen storage ability and oxygen mobility of the catalyst. Among all the catalysts, 0.5 wt% Pd/5 wt% ZrO₂/SBA-15 exhibited the best catalytic performance and stability. After 400 h

of an on-stream reaction at 450 °C, the methane conversions remained unchanged. Ruiz et al. investigated the catalytic activities of the MCM-41-supported Pd catalysts for methane combustion [67]. Although the change in structure was not observed, the addition of La or Ce gave rise to a decrease in the catalytic activity of the methane combustion, and the all-silicate-based catalyst was more active than the Pd sample supported on aluminosilicate. In addition, the hydrophobic nature of the support and the reducibility of PdO were the main factors influencing the performance of the catalyst.

Peng et al. developed a facile in situ mesoporous-free strategy to synthesize Pd NPs enveloped in a single-crystal S-1 zeolite with intra-mesopores (Pd@IM-S-1) [68]. The Pd@IM-S-1 catalyst exhibited good performance for the deep oxidation of light alkanes (the $T_{90\%}$ was as low as 318 °C for CH₄ combustion), which was attributable to the confinement effect of the zeolite shell and improvement in the mass transfer efficiency and accessibility of the active metal sites. The Pd-PdO interface as a new active site could provide the active oxygen species for cleavage of the first C–H bond in light alkanes. It is proved that the restriction of zeolite channels further protects PdO NPs from sintering or hydrothermal aging under methane oxidation conditions, giving rise to high catalytic activity, stable operation durability, and good high-temperature stability. However, what can confine the active site is still controversial. In short, all kinds of zeolite supports with different skeleton architectures and pore diameters (i.e., micro- and mesopores) are suitable as supports of the Pd-based catalysts for CH₄ combustion.

2.5. Other Noble Metal-Based Zeolite Catalysts

Rh has been far less studied for CH_4 combustion, but it is an important component in the three-way catalysts, which can improve the catalytic activity and stability of the catalysts. Christensen et al. examined the impacts of temperature and SO₂ concentration (1–20 ppm) on the activity of the catalysts [69]. The deactivation induced by sulfur dioxide introduction was intensified with the drop in temperature or the rise in SO₂ concentration, and such a SO_2 poisoning could be thought to be due to partial or complete occupation of the active sites (which exhibits a Temkin adsorption isotherm). In the presence of 1–2 ppm SO₂, full coverage of the S-containing species was reached at 400 $^{\circ}$ C, but the coverage was significantly decreased at 500 °C, and significant catalytic activity was retained in the presence of SO₂. Recently, the same group reported that the 2 wt% Rh/ZSM-5 catalyst showed high methane conversions at high space velocities in the presence of water and sulfur dioxide [70]. The Rh-based catalysts with the presence of Rh₂O₃ were superior to the Pd-based catalysts in the presence of H₂O and SO₂. Although both water and sulfur dioxide decreased the activities of the supported Pd and Rh catalysts, water was found to exert a destabilizing effect on rhodium sulfate, i.e., the presence of water caused the sulfate to be partially decomposed below 400 °C, which could partly alleviate the sulfur dioxide poisoning of the supported Rh catalysts. The combined inhibition derived from $(H_2O + SO_2)$ was weaker for the supported Rh catalysts than that for the supported Pd catalysts. In fact, the research works on CH₄ combustion over the supported Rh catalysts are relatively insufficient in the literature. In addition to the aluminosilicate zeolites, the silico-alumino-phosphate (SAPO) molecular sieves were also thought to be promising support materials. Nomura et al. studied CH₄ combustion over the Pd-SAPO-5 catalyst and found that steam strongly inhibited methane combustion [71]. Under the same conditions (10 vol% water vapor), the bimetallic Pd-Pt-SAPO-5 catalyst showed better methane combustion activity after the doping of Pt. Osman et al. investigated that the four-component catalyst containing bimetallic Pt and Pd NPs (for stability), TiO₂ (for oxygen mobility), and η -Al₂O₃ or H-ZSM-5 (acidic support) was superior to the simpler catalysts [72]. The multi-component catalyst with the optimized parameters obviously promoted the enhancement in methane combustion activity ($T_{90\%}$ = 200 °C at a GHSV of 10,000 mL/(gh), and the long-term fluidization experiment showed that the activity of the catalyst did not decrease after more than 50 h of reaction at 250 °C. Meanwhile, Dai et al. prepared the PdO/CeO_2 nanosheets wrapped by the HZSM-5 film hybrid composite

with sandwich and core-shell structures [73]. The as-synthesized materials exhibited excellent catalytic performance for methane combustion ($T_{90\%} = 495$ °C, turnover rate (TOR) = 0.618 s⁻¹), and the HZSM-5 coating improved the resistance to sintering, oxygen, and water, while severe sintering of the conventionally prepared PdO/CeO₂ catalyst was suffered at high temperatures or oxygen concentrations. These results demonstrate that the multi-component catalysts possess better stability than the single Pd catalysts, and the doping of a suitable metal may stabilize the activity of the Pd-based catalyst. In practice, the design of a multi-component catalyst is beneficial for the enhancement of the low-temperature combustion of methane.

So far, the topological structure of a zeolite does not play the most important role in governing the activity of the zeolite-based catalyst for CH₄ combustion. Researchers are more inclined to control the molecular sieve in a beneficial way so as to obtain a high and stable methane oxidation catalyst with better performance.

Zeolite Framework	Catalyst	Catalyst Preparation Method	Pd Loading (wt%)	Feed Gas	GHSV ^a (mL/(gh))	T _{50%} /T _{90%} ^b (°C)	TOF ^c (×10 ⁻² s ⁻¹)	Ref.
MFI	Pd/ZSM- 5(14)	Ion exchange	3.39	$1 \text{ vol}\% \text{ CH}_4 + 21 \text{ vol}\% \text{ O}_2 \\ + \text{N}_2 \text{ (balance)}$	60,000	260/275	1.3	[50]
MFI	Pd/Na-ZSM- 5	Ion exchange	4.84	$\begin{array}{l} 1 \text{ vol}\% \text{ CH}_4 + 18 \text{ vol}\% \text{ O}_2 \\ + \text{N}_2 \text{ (balance)} \end{array}$	60,000	285/290	1.2	[74]
MFI	Pd/ZSM-5	Ion exchange	0.1	$0.2 \text{ vol}\% \text{ CH}_4 + 18 \text{ vol}\%$ $O_2 + N_2 \text{ (balance)}$	120,000	370/>650	-	[75]
MFI	Pd/ZSM-5	Impregnation method	0.55	$0.2 \text{ vol}\% \text{ CH}_4 + 10 \text{ vol}\%$ $O_2 + N_2 \text{ (balance)}$	72,000	332/373	-	[76]
MFI	Pd/Silicalite- 1	Ion exchange	0.96	$1 \text{ vol}\% \text{ CH}_4 + 10 \text{ vol}\% \text{ O}_2 \\ + \text{ Ar (balance)}$	$3000 \ h^{-1}$	286/347	-	[77]
MFI	Pd/S-1-in- 6EN	One pot	0.93	$1 \text{ vol}\% \text{ CH}_4 + 20 \text{ vol}\% \text{ O}_2 \\ + \text{N}_2 \text{ (balance)}$	60,000	-/364	4.1	[78]
FAU	PdMo/Y- zeolite	Ion exchange	2	$1 \text{ vol}\% \text{ CH}_4 + 4 \text{ vol}\% \text{ O}_2 + \text{He (balance)}$	120,000	410/-	-	[58]
FAU	Pd/Y-zeolite	Ion exchange	2.5	$1 \text{ vol}\% \text{ CH}_4 + 4 \text{ vol}\% \text{ O}_2 \\ + \text{He (balance)}$	100,000	415/-	-	[79]
CHA	Pd/SZZ-13	Ion exchange	1.1	$0.15 \text{ vol}\% \text{ CH}_4 + 5 \text{ vol}\%$ $O_2 + \text{He} \text{ (balance)}$	200,000	317/-	1.7	[80]
LTA	Pd/LTA	Ion exchange	1.0	$0.15 \text{ vol}\% \text{ CH}_4 + 5 \text{ vol}\% \text{ O}_2 + \text{He (balance)}$	200,000	447/-	1.5	[80]
LTA	Pd/LTA	Impregnation method	2.12	$0.05 \text{ vol}\% \text{ CH}_4 + 8 \text{ vol}\%$ $O_2 + \text{Ar} \text{ (balance)} + 5 \text{ vol}\% \text{ H}_2\text{O}$	27,200	388/-	-	[48]
CHA	Pd/SSZ-13	Impregnation method	1.06	$0.05 \text{ vol}\% \text{ CH}_4 + 5 \text{ vol}\%$ $O_2 + \text{Ar} \text{ (balance)}$	$13,600 \ h^{-1}$	311/-	-	[81]
BEA	Pd/Beta-40	Impregnation method	1.0	$\begin{array}{l} 0.05 \text{ vol}\% \text{ CH}_4 + 5 \text{ vol}\% \\ \text{O}_2 + \text{Ar (balance)} \end{array}$	$13,600 \ h^{-1}$	281/-	-	[81]
BEA	RD-Pd/D- Beta	Reduction deposition	0.5	$1 \text{ vol}\% \text{ CH}_4 + 21 \text{ vol}\% \text{ O}_2 \\ + \text{N}_2 \text{ (balance)}$	30,000	333/< 375	-	[55]
BEA	Pd(0.5)Co(1.0) /BEA	Impregnation method	0.5	$0.15 \text{ vol}\% \text{ CH}_4 + 5 \text{ vol}\%$ $O_2 + \text{Ar} \text{ (balance)}$	99,900	352/420	-	[82]
BEA	Pd/Beta-SH- HT	Mercaptosilane assisted	0.5	1 vol% CH ₄ + 21 vol% O ₂ + N ₂ (balance)	30,000	290/333	-	[56]
CHA	Pd/SAPO- 11	Ion exchange	1.1	$0.4 \text{ vol}\% \text{ CH}_4 + 10 \text{ vol}\%$ $O_2 + N_2 \text{ (balance)}$	50,000	320/-	-	[71]
MOR	Pd/Na- MOR	Ion exchange	1.0	$1 \operatorname{vol} CH_4 + 4 \operatorname{vol} O_2$ + N ₂ (balance)	70,000 h^{-1}	335/< 420	-	[57]
Meso-pore	Pd/MCM-41	Impregnation method	1.36	2.5 vol% CH_4 + 10 vol% O_2 + Ar (balance)	60,000	386/-	-	[67]
Mesopore	Pd/MCM-41	Grafting	1.0	$1 \text{ vol}\% \text{ CH}_4 + 4 \text{ vol}\% \text{ O}_2 \\ + \text{He (balance)}$	120,000	409/-	-	[64]
Meso-pore	Pd-5 wt% CeO ₂ /SBA- 15	Impregnation method	1.0	$\begin{array}{l} 2 \text{ vol}\% \text{ CH}_4 + 21 \text{ vol}\% \text{ O}_2 \\ + \text{ N}_2 \text{ (balance)} \end{array}$	72,000	342/406	1.64	[66]
Meso-pore	Pd-5 wt% ZrO ₂ /SBA- 15	Impregnation method	0.5	$\begin{array}{l} 2 \operatorname{vol}\% \operatorname{CH}_4 + 21 \operatorname{vol}\% \operatorname{O}_2 \\ + \operatorname{N}_2 \text{ (balance)} \end{array}$	72,000	322/364	1.22	[66]

 Table 2. Summary of the zeolite-supported Pd-based catalysts for complete oxidation of methane.

Zeolite Framework	Catalyst	Catalyst Preparation Method	Pd Loading (wt%)	Feed Gas	GHSV ^a (mL/(gh))	T _{50%} /T _{90%} ^b (°C)	TOF ^c (×10 ⁻² s ⁻¹)	Ref.
Meso-pore	Pd- CeO ₂ /SBA- 15	Impregnation method	5%	0.1 vol% CH_4 + 10 vol% O_2 + Ar (balance)	180,000	290/<360	-	[83]
Meso-pore	Pd@IMS-1	Dry-gel conversion	1.83	$1 \text{ vol}\% \text{ CH}_4 + 20 \text{ vol}\% \text{ O}_2 \\ + \text{ N}_2 \text{ (balance)}$	36,000	261/318	1.5	[68]
MFI	Pd/HZSM-5	Impregnation method	2.0	$1 \text{ vol}\% \text{ CH}_4 + 4 \text{ vol}\% \text{ O}_2$ + N ₂ (balance)	30,000	-/400	-	[84]
MFI	Pd/TS-1	Impregnation method	1.4	$0.7 \text{ vol}\% \text{ CH}_4 + 20 \text{ vol}\%$ $O_2 + N_2 \text{ (balance)}$	200,000	-/430	0.7	[85]
MFI	Pd/HZSM-5	Impregnation method	1	0.7 vol% CH ₄ + 20 vol% O ₂ + N ₂ (balance) + 3 vol% H ₂ O	200,000	-/-	4.1	[86]
MFI	Pd/S-1-in	In situ method	0.123	$1 \text{ vol}\% \text{ CH}_4 + 20 \text{ vol}\% \text{ O}_2 \\ + \text{ N}_2 \text{ (balance)}$	16,000	329/382	3.22	[87]
MFI	Pd@S-1	Hydrothermal method	0.6	$1 \text{ vol}\% \text{ CH}_4 + 16 \text{ vol}\% \text{ O}_2 \\ + \text{ N}_2 \text{ (balance)}$	50,000	323/<380	2.6	[53]
MFI	Pd@H-ZSM- 5	Hydrothermal method	0.7	$1 \text{ vol}\% \text{ CH}_4 + 5 \text{ vol}\% \text{ O}_2 \\ + \text{He (balance)}$	$60,000 \ h^{-1}$	350/400	-	[88]
MFI	PdCo@MFI	One-pot synthesis	0.54	$1 \text{ vol}\% \text{ CH}_4 + 20 \text{ vol}\% \text{ O}_2 \\ + \text{ N}_2 \text{ (balance)}$	30,000	-/<400	-	[89]
MFI	Pd/NaLa- ZSM-5	Impregnation method	2.0	$0.15 \text{ vol}\% \text{ CH}_4 + 5 \text{ vol}\%$ $O_2 + N_2 \text{ (balance)}$	60,000	264/296	-	[90]
MFI	Pd/ZSM-5- Si	Colloidal immersion	1.0	$0.15 \text{ vol}\% \text{ CH}_4 + 5 \text{ vol}\%$ O ₂ + N ₂ (balance)	60,000	288/331	-	[91]

Table 2. Cont.

^a GHSV refers to the corresponding gas hourly space velocity of the catalytic reaction system; ^b the temperatures ($T_{50\%}$ and $T_{90\%}$) at which methane conversions reached 50 and 90%, respectively; ^c turnover frequency (TOF) provided by the corresponding references.

3. Physicochemical Parameters

3.1. Active Site and Metal Particle Size

For the zeolite-supported Pd-based catalysts for CH₄ combustion, the metal loadings are usually below 5 wt%. Traditional preparation processes, such as ion exchange, precipitation, and calcination after impregnation, often lead to metal NPs being dispersed on the outer surface of the supports. Up to now, PdO has been the main active site for methane combustion reported in most of the literature. Wang et al. prepared the Pd NPs embedded in S-1 (Pd@S-1) with Pd loadings of 0.3-1.6 wt% [53]. The 0.6Pd@S-1 catalyst performed the best, with a total conversion of CH₄ being achieved at 380 °C. However, the 0.6Pd/S-1 and 0.6Pd/ZSM-5 samples derived through the IWI approach showed substantially higher $T_{100\%}$ values of ca. 470 and 465 °C under the same reaction conditions (Figure 2), respectively. Furthermore, the apparent activation energy (E_a) over the 0.6Pd@S-1 catalyst was lower than those over the other catalysts, suggesting that the Pd site inside S-1 exhibited higher intrinsic activity. Petrov et al. claimed that Si/Al could determine the size distribution of the particles, because acidity controlled the mobility and dispersion of palladium oxide [57]. These authors also pointed out that a low Si/Al ratio led to a good metal dispersion. Conversely, a high Si/Al ratio typically gives rise to good stability and high hydrophobicity. For the zeolite-supported catalysts used for methane oxidation, bimetal NPs are remarkably more active than the single-metal NPs. For example, Chen et al. reported that occupying the exchange sites with other metal ions (e.g., Co^{2+}) also reduced the probability of the Pd reaching the exchange site, leading to the formation of PdO NPs, which resulted in a catalyst with higher CH_4 combustion activity [82]. In addition, the CH₄ conversion over Pd_{0.5}Co_{1.0}/BEA at 250 °C was 77% (which was higher than that over $Pd_{1,0}$ /BEA), indicating that the amount of Pd was greatly reduced.



Figure 2. (a) Methane conversions versus temperature over the Pd@S-1 catalysts with various Pd loadings, and (b) the dependence of TOF values on the size of PdO NPs in the Pd@S-1 catalysts at 280 °C. Reaction conditions: $1 \text{ vol} \otimes \text{CH}_4 + 16 \text{ vol} \otimes \text{O}_2 + \text{N}_2$ (balance), and GHSV = 50,000 mL/(g h). Reproduced from Ref. [53] with permission from Elsevier.

Although small NPs expose a higher proportion of the unsaturated active sites, larger particles are preferred in some cases. Pd NPs within a certain size range have been confirmed to show the best activity for the total oxidation of methane. For example, Fan et al. synthesized the Pd/H-ZSM-5 catalysts and exposed them to different treatments (e.g., calcination, reduction, and oxidation) to alter the particle sizes [92]. These authors found that the TOFs of the catalysts for methane oxidation displayed a volcanic relationship with the size of Pd particles and reached the highest activity at ca. 5 nm. Recently, Liu et al. synthesized Pd@S-1 using the different ethylenediamine (EN) ligand contents and investigated the effect of the EN amount on particle size [78]. A volcano-shaped relationship between the step site fraction by size control of Pd NPs and the catalytic activity was observed. The most active catalyst contained the optimal Pd NPs with a size of 2.1 nm. Generally speaking, a higher metal loading gives rise to a larger size of metal NPs, although the fabrication approach is a critical factor. Typically, the ion exchange (followed by calcination) produces metal NPs in the size range of 1–1.5 nm, in situ encapsulation with ethylenediamine leads to metal NPs in the size range of 1–3 nm, and impregnation generates relatively large NPs with particle sizes of 3-40 nm. After synthesis by impregnation, hydrothermal treatment is sometimes adopted to reduce the particle size of the metal. Usually, the first two methods produce small and stable metal NPs located within the zeolite micropores. However, simple impregnation usually gives rise to larger metal NPs outside the micropores of the zeolite. The precise control of metal NPs-loaded molecular sieves is beneficial for the synthesis of efficient low-temperature catalysts for methane combustion.

3.2. Si/Al Ratio and Acid Site

It was reported that the Si/Al ratio of ZSM-5 could affect water resistance of a noble metal catalyst due to the good hydrophobicity of ZSM-5 with a higher Si/Al ratio [93]. The results of early studies carried out in the 1990s revealed a general trend that the CH₄ combustion activity and stability of the Pd/zeolite catalysts increase with the rise in the Si/Al ratio (>1200) of the zeolite support, and the resulting catalysts exhibit significantly improved activity and on-stream durability at low temperatures. It has been claimed that strong solid acids and Brønsted acidic sites may directly assist the activation of C–H bonds in CH₄. For example, Gao et al. adopted the in situ hydrothermal method to encapsulate the cationic Pd sites inside the MFI-type zeolite [88]. Within the constrained environment of the MFI zeolite, the existence of the Brønsted acidic sites can promote CH₄ activation at the Pd sites. The parent H-ZSM-5 zeolite was entirely inactive for CH₄ oxidation below 500 °C, but adding the Pd species through the in situ fabrication or wet impregnation could effectively enhance CH₄ oxidation below 500 °C. The acidic H-ZSM-5 zeolite offered

a superior carrier for the active Pd species compared with the basic Na-ZSM-5 zeolite. Furthermore, Pd@H-ZSM-5 and Pd/H-ZSM-5 exhibited significantly higher activities than Pd@Na-ZSM-5 and Pd/Na-ZSM-5, respectively. It is evident that the Brønsted acid sites assist the activation of CH₄ at the Pd sites and lower the energy barrier. The collaboration between the Pd site and the adjacent Brønsted acid site is beneficial for the activation of CH₄. Figure 3 shows the T_{50} as a function of the Al/(Al + Si) ratio in different zeolite materials, which shows an obvious anti-volcanic shape. On the contrary, it has also been suggested that the Lewis acid can intensify the interaction between Pd species and H-ZSM-5, inhibiting the agglomeration of Pd particles (i.e., improving the dispersion of Pd species), and thus enhancing the catalytic performance of Pd/H-ZSM-5 in CH₄ combustion [94]. In a word, a high Si/Al ratio in a catalyst seems to favor the reduction in sintering and deactivation due to water. It also requires more complex fabrication procedures (including various pretreatments and post-treatments) to well disperse the active metal(s).



Figure 3. T_{50} (temperature at a methane conversion of 50%) values with experimental error bars for the set of different zeolites tested in the presence of water in the stream. Dotted lines are added as a guide to the eye. Reproduced from Ref. [95] with permission from the American Chemical Society.

3.3. The Presence of Alkaline Metal Counter Ions

It has been recognized that the alkali metal hydroxides (MeOH, Me = Li, Na, K, or Cs) may play the role of an electronic or textural stimulant to change the electron density and dispersion of the noble metal(s), hence enhancing the effectiveness of the noble metal catalysts. For instance, Wang et al. used various MeOH (Me = Li, Na, K, and Cs) compounds as the precipitants to generate the Pd/H-ZSM-5-Me catalysts via a deposition precipitation route and investigated the effect of the alkali metal ion on the catalytic activity of Pd/H-ZSM-5 for the lean CH_4 combustion [96]. The results indicate that in comparison with ammonia, alkali metal hydroxides as the precipitants could significantly improve the catalytic activity of Pd/H-ZSM-5 in lean CH_4 combustion. The doping of an alkali metal decreased the $T_{90\%}$ significantly (e.g., from 379 °C (over Pd/H-ZSM-5) to 304 °C (over Pd/H-ZSM-5-Cs)). The alkali metal ion could improve the dispersion of the Pd species on H-ZSM-5 and reduce the size of the Pd particles. Moreover, the Me ion may serve as an electron-donating medium and endow the Pd species with a unique electronic characteristic (which could favor the activation of C–H bonds in methane) (Figure 4). Recently, Xie et al. have pointed out that the zeolite-supported Pd catalysts exhibited pronounced discrepancies in the catalytic activity of CH₄ combustion when Na-ZSM-5 was ion-exchanged with the La, Ni, or Mg ion [90]. Interestingly, the Pd/NaLa-ZSM-5 catalyst showed the best activity. Over the best-performing catalyst, total CH₄ conversion could be

achieved at around 320 $^{\circ}$ C, which was ca. 60 $^{\circ}$ C lower than the temperature required over the Pd/Na-ZSM-5 catalyst.



Figure 4. (a) Free energy profiles for the dissociation of the first C–H bond in methane over various supported palladium catalysts and (b) light-off profiles of methane combustion over various H-ZSM-5-supported palladium catalysts (Pd/H-ZSM-5, Pd/H-ZSM-5-Li, Pd/H-ZSM-5-Na, Pd/H-ZSM-5-K, and Pd/H-ZSM-5-Cs) at 1.0 vol% CH₄ in air and GHSV = 30,000 mL/(g h). Reproduced from Ref. [96] with permission from Elsevier.

3.4. Incorporation of a Second Base Metal

The doping of a second metal to Pd/zeolite has been demonstrated to enhance the CH₄ combustion performance at low temperatures. For example, Shi et al. prepared the Pd-M/HZSM-5 catalysts (Si/Al = 165, M = Ce, La, Sm, Nd, and Tb) via the impregnation of HZSM-5 [97]. It was found that Pd-Ce/HZSM-5 exhibited the best catalytic activity at a GHSV of 48,000 h^{-1} . In the presence or absence of 4 vol% water vapor, the Pd-Ce/HZSM-5 catalyst had a significantly lower tendency to be deactivated compared with the Pd/HZSM-5 catalyst. The best performance was due to the fact that the doping of CeO₂ could enhance the re-oxidation of Pd on Pd-Ce/HZSM-5 through providing the active oxygen species, maintaining the appropriate oxidation state of the Pd active sites under the adopted reaction conditions, and hence increasing the amount of the reactive PdO species on Pd-Ce/HZSM-5. Meanwhile, these authors doped the metal (Zr, Zn, Cu, La, Ba, Fe, Mn, Ca, Mg, or Li) oxide to Pd/HZSM-5 via the impregnation route and investigated their catalytic performance for methane oxidation at low temperatures [98]. ZrO₂ was found to be a suitable dopant for the enhancements in catalytic activity and stability of the supported palladium catalyst. The temperatures for methane ignition $(T_{10\%})$ and total conversion $(T_{100\%})$ over Pd-Zr/HZSM-5 were 25 and 55 °C lower than those over Pd/HZSM-5, respectively. Furthermore, the results of oxygen temperatureprogrammed desorption (O₂-TPD) and methane temperature-programmed reduction (CH₄-TPR) (Figure 5) revealed that the temperatures for O₂ desorption and reduction by CH₄ of the catalysts decreased with the increase in catalytic activity. Hence, the presence of a greater amount of the active PdO_x species on Pd-Zr/HZSM-5 was thought to be the main reason for its significantly enhanced catalytic activity (Figure 5). These findings were in good consistency with the results reported by Niu et al. [87] and Shi et al. [97]. Dopants, such as CeO₂, ZrO₂, and TiO₂, were found to exert remarkable positive effects [66,82,99,100]. The ideal zeolite is relatively hydrophobic and has low acidity, either from a high Si/Al ratio or the exchange of the remaining H⁺ with alkali metal counterions (e.g., Na⁺), and the high Si/Al ratio in the catalyst seems to be beneficial for reducing sintering and deactivation due to water. It also needs more accurate manufacturing procedures (including various pretreatments and post-treatments) to well disperse the active metals. In the lowtemperature combustion of CH_4 over the Pd-based catalysts, there is a consensus that methane combustion must require the participation of PdO, which is the active phase in



CH₄ combustion, so the second metal can precisely regulate the strength of the Pd-O bond to achieve the low-temperature combustion of methane.

Figure 5. CH₄-TPR profiles of different catalysts heated in a mixture (15 mL/min) of 4.0 vol% CH₄ + He (balance) at a heating rate of 20 °C/min. Reproduced from Ref. [99] with permission from the Royal Society Chemistry.

4. Effects of Water and Sulfur Dioxide on Catalytic Performance

Under the actual operation conditions, the catalytic combustion of methane and unburned low-concentration methane can produce water, which exerts a strong inhibitory effect on the activity of the adopted catalyst. Water can inhibit CH_4 oxidation by changing the structure of the active phase in the catalyst. For example, Barrett et al. observed the formation of the $Pd(OH)_2$ inactive phase in Pd/Al_2O_3 during the wet CH_4 oxidation using temperature-programmed in situ X-ray absorption spectroscopy [101]. Another point of view is that H_2O or the spillover of the H-containing species can block the active sites. As reported by Persson et al., the covering impact of OH was the main reason for the deactivation of Pd/Al_2O_3 [102]. The inhibitory effect of water can be more obvious at low temperatures where the catalysts are active, because the high active site coverage by water is favored at low temperatures.

On the basis of the above enlightening idea, many water-resistant catalysts were developed. The influence of water vapor on the activity of the Pd-based catalysts depends upon the alteration in the physicochemical property of the support [14]. Generally speaking, the stability of a catalyst in the wet atmosphere increases with the hydrophobicity of the adopted support [103]. The unique framework structure of a zeolite support shows the considerable hydrothermal stability of the confinement impact to noble metal(s). Losch et al. prepared the multiporous zeolites with different hydrophobic/hydrophilic characteristics and studied the relationship between the activation energy of the catalyst and the hydrophilicity of the zeolite by loading Pd NPs prepared in advance on zeolite [95]. The optimal catalyst was Pd NPs (3.2 nm in particle size) supported on a mesoporous zeolite or USY with a Si/Al ratio of 40, which exhibited a $T_{50\%}$ of 355 °C and a $T_{90\%}$ of 375 °C under the steam-containing reaction conditions. Based on the obtained results, the authors proposed an appropriate explanation that the acidic sites were required to remove the water generated by methane combustion.

Under the wet conditions, the cage-based and small-pore zeolites are more effective supports for loading Pd than the channel-based and medium-pore ZSM-5 zeolite (which is one of the most extensively investigated zeolite supports for methane combustion). For instance, Li et al. used the ligand to stabilize the Pd in the zeolite synthesis and realized the encapsulation of the well-dispersed PdO clusters (1.8–2.8 nm) in microporous channels and voids of the S-1 support [104]. The synthesis condition of such a catalyst influenced the encapsulation extent and particle size distribution of the noble metal. Due to the encapsulation impact of the small PdO clusters and the inherent properties (i.e., low acidity, high hydrophobicity, and good hydrothermal stability) of S-1, the optimized

Pd@S-1 catalyst outperformed the traditional Pd-based counterparts derived from the wetness impregnation route, and the former exhibited both higher catalytic performance and better thermal stability in the lean CH₄ combustion. Tang et al. incorporated the Co species to channels of the MFI-type zeolite to promote the activation of the surface oxygen species and modify the electronic state of the Pd species [89], which increased its catalytic activity for CH₄ combustion at low temperatures in the presence of water (Figure 6a,b). The PdCo particle size was not significantly increased, and the catalytic activity of PdCo@MFI was stable after 20 h of reaction at 420 °C in the presence of water (Figure 6c), which was much more stable than PdCo/ZSM-5 and PdCo/Al₂O₃ (over which methane conversions were decreased by 19 and 22%, respectively). The recent literature on methane combustion reported that molecular sieves with high Si/Al ratios (SARs) seemed to be needed for methane combustion, in which structures of the molecular sieves were considered under the hydrothermal conditions. Therefore, a more thorough investigation on the structure integrity of a zeolite support is highly relevant under the realistic conditions of methane combustion.



Figure 6. (a) The catalytic activity and (b) stability test of various catalysts. Reaction condition: 1 vol% CH₄ + 20 vol% O₂ + 5 vol% H₂O + N₂ (balance). Reproduced from Ref. [89] with permission from Elsevier. (c) Influence of operation temperature (450, 475, and 500 °C) on activity of the 2 wt% Rh/ZSM-5 catalyst in the presence of 0–20 ppm SO₂. Test conditions: 2500 ppm CH₄ + 10 vol% O₂ + 5 vol% H₂O + 1, 2, 5, 10, or 20 ppm SO₂ (when present) + N₂ (balance), GHSV = 150,000 mL/(g h). Reproduced from Ref. [69] with permission from Elsevier.

Usually, sulfur dioxide is present in the natural gas stream or in the automotive exhaust from natural gas engines or turbines, even if its concentration is very low. The SO₂ resistance of a catalyst remains a key issue. Supported noble metal catalysts are easily poisoned when they are exposed to the sulfur dioxide-containing gas mixture derived from natural gas combustion. For example, the irreversible deactivation induced by SO₂ is due to its occupation of the active sites and/or transformation of the highly active PdO phase in the catalyst to the less active PdSO₃ or PdSO₄ species. Similar outcomes were also obtained in the other works [105–107].

Although the high cost of Rh may limit its practical applications, this element is an important component in the three-way catalysts (because it can improve catalytic activity and stability). Recently, Zhang et al. observed that the water vapor effect on activity could be weakened over the ZSM-5-supported 2 wt% Rh catalyst [69]. As can be seen from Figure 6c, the $T_{90\%}$ values over Rh/ZSM-5 and Pd/ZSM-5 were 525 and 575 °C in the presence of H₂O and SO₂, respectively. The results of TPD characterization revealed that water could destabilize the rhodium sulfate species, giving rise to its partial decomposition at temperatures lower than 400 °C. The combined inhibitory effect of (H₂O + SO₂) on the activity of the supported Rh catalyst was weaker than that of the supported Pd catalyst (in which such an effect was irreversible). Figure 7 shows the density function theory (DFT) model of water adsorbed at the unsaturated Pd atom of a clean PdSO₄ surface proposed by Auvinen et al. [108].



Figure 7. Energy profiles (solid line) predicted by the NEB and the associated Bader charges (dashed lines) for dissociation of methane to the S_2 position on a clean PdSO₄(111) surface and a hydroxylated PdSO₄(111) surface. The black bars on the energy curve denote minimum and TS structures, whereas small diamonds denote NEB images. The green bar denotes the energy of the final structure with reoriented hydroxyl groups. Negative Bader charge corresponds to an excess of electrons relative to isolated atoms, whereas positive Bader charge corresponds to the deficiency of electrons. Reproduced from Ref. [108] with permission from the American Chemical Society.

In addition, water vapor introduction accelerates the poisoning of the Pd-based catalysts by sulfur dioxide, and the possible mechanisms are shown in Figure 8 [109]. Under dry conditions, sulfur dioxide can be adsorbed on alumina or Pd and migrate between the metal and the support via surface diffusion. On PdO, part of the SO₂ can be oxidized to SO₃ and form PdSO₄ or overflow on the support, causing the catalyst to be sulfated. Due to the capture and storage of SO₂ and SO₃ by the support, the sulfation rate of Pd and the deactivation rate of PdO are lower. Water can suppress the capture of SO₂ by Al₂O₃ through reducing the number of sites available for SO₂ adsorption. As a result, sulfur dioxide adsorbed on PdO does not overflow to the surface of Al₂O₃ but is oxidized to SO₃ that in turn increases the formation of PdSO₄.



Figure 8. Schematic diagram of the possible mechanism of sulfur poisoning in the absence or presence of water vapor. Reproduced from Ref. [109] with permission from Elsevier.

In a word, sulfur dioxide itself is not the only reason for the deactivation of the catalysts for methane combustion, but catalyst deactivation is a combined effect of water vapor and sulfur dioxide. The irreversible poisoning of sulfur dioxide undermines the mobility of oxygen and hinders the desorption of water, which decreases the activity of methane combustion at low temperatures. It is highly necessary to prevent the transformation of the PdO active phase and improve SO_2 tolerance by introducing dopants, alloying, and redox active metal oxides (e.g., CeO₂).

5. Deactivation by Sintering

Compared with other precious metals catalysts, the Pd-based ones show better catalytic activities for CH_4 combustion, except that the latter catalysts are deactivated due to the presence of SO_2 and a lot of water vapor in the exhaust gas as described above. One weakness of supported PdO catalysts is that its active phase PdO decomposes into metallic Pd0, and Pd NPs are aggregated into large Pd particles at high temperatures (this phenomenon is called sintering), which leads to a significant decline in catalytic activity. Under the guidance of the assumption that PdO NPs are the active sites for CH4 combustion, some works have been conducted to directly introduce Pd NPs into zeolites so as to study where the PdO particles were located and how they interacted with the zeolitic supports [35,110]. Therefore, it is very necessary to investigate how to stabilize the PdO active phase and improve the stability of the catalyst. Not only may the temperature-programmed activity of methane oxidation decrease obviously but also transmission electron microscopy (TEM) can be employed to analyze the causes of catalyst deactivation.

Generally speaking, it is possible to improve the thermal stability of a catalyst by tuning its composition and metal—support interaction or loading the active metal NPs on an ordered mesoporous or core-shell-structured material [21,111,112]. A more recently developed strategy has been to encapsulate the active metal NPs inside the framework of a microporous zeolite [113,114]. As mentioned earlier, sintering due to a hydrothermal treatment becomes a problem. It has also been reported that if the Al concentration of a zeolite is too high, it is easy to dealuminate in the presence of H_2O , which eventually leads to the growth of Pd particles. Therefore, high-performance and stable catalysts can be obtained by adjusting the Si/Al ratios and carefully selecting zeolite materials. Moreover,

the active metal particles should be uniformly dispersed and preferably encapsulated in zeolite to prevent the sintering induced by particle aggregation.

6. Catalytic Methane Combustion Mechanism

For the low-temperature CH_4 combustion over the supported Pd catalysts, it is a consensus that PdO is involved in the combustion of methane. PdO is the active phase in the reaction, while pure Pd particles are basically inactive. Although some researchers believe that the reduced metallic Pd⁰ particles can promote methane combustion to some extent, they also insist that it is difficult to carry out methane combustion without the joint participation of PdO [88,115].

Under the condition of low-temperature methane combustion, PdO is stable, and most researchers believe that CH₄ combustion over the supported Pd catalysts obeys a redox mechanism, i.e., the MvK mechanism. According to this mechanism, methane first adsorbs on PdO, reacts with the lattice oxygen of PdO (i.e., PdO is reduced), and then the reduced Pd reacts with oxygen molecules to be oxidized to PdO. In order to confirm that the lattice oxygen of PdO participates in methane combustion, Muller et al. conducted the 18 O isotope experiment. First, the original Pd/ZrO₂ support was thermally treated in ¹⁸O-containing Ar at 500 °C to obtain Pd¹⁸O/ZrO₂, and then PdO and (1.0 vol% CH₄ + 4 vol% O₂) were reacted through the pulse experiment [116]. The results showed that all the CO₂ produced after the first pulse reaction was $C^{18}O_2$. With the increase in pulse reaction times, the calculation results of the final reaction products revealed that there was at least 20 vol% C¹⁸O₂ in total CO₂ production. This result demonstrated that the above redox mechanism existed in methane combustion. In addition, many research groups also confirmed the participation of lattice oxygen in PdO in methane combustion using the oxygen isotope tracing technique, and methane combustion was completed via a similar redox mechanism [117–119]. The above results show the importance of the MvK mechanism in CH_4 combustion.

In addition, Iglesia and coworkers also proposed a modified mechanism of methane combustion, as shown in Schemes 1 and 2 [120]. They thought that methane was first adsorbed on Pd (-oxygen vacancies) which was coordinately unsaturated on the surface of PdO, then reacted with the neighboring PdO to generate the adsorbed CH_3 and OH species, and finally the H on the CH_3 was seized by the neighboring PdO in turn to generate the OH species. The rupture of the first C–H bond in the CH_4 was considered to be the rate-determining step of this process. This mechanism introduces the concept of oxygen vacancies on the PdO surface, thus avoiding the need for the coexistence of metallic Pd^0 and PdO in methane combustion. Because there is a large amount of excessive oxygen in the reaction gas in the actual continuous methane combustion, it is difficult to imagine that real metallic Pd^0 particles can be generated on the catalyst surface.



Scheme 1. Methane dissociation on a surface Pd-PdO site pair. Reproduced from Ref. [120] with permission from Elsevier.

$$O_{2} + * \xleftarrow{K_{1}} O_{2} *$$
(1)

$$O_{2} + * \xleftarrow{K_{2}} 2O *$$
(2)

$$CH_{4} + * \xleftarrow{K_{3}} CH_{4} *$$
(3)

$$CH_{4} + O^{*} \xleftarrow{K_{4}} CH_{3} * + OH^{*}$$
(4)

$$\dots \longrightarrow \dots$$

$$2OH^{*} \xleftarrow{K_{5}} H_{2}O(g) + O^{*} + *$$
(5)

$$CO_{2}^{*} \xleftarrow{K_{6}} CO_{2} + *$$
(6)

$$CO_{3}^{*} \xleftarrow{K_{7}} CO_{2} + O^{*}$$
(7)

Scheme 2. Proposed reaction pathways for the oxidation of methane on PdO_x crystallites. Reproduced from Ref. [120] with permission from Elsevier.

Although PdO is usually regarded as the catalytically active phase in methane combustion, it is difficult to effectively characterize the Pd species in actual methane combustion. Hence, the specific behavior characteristics of the Pd species in actual CH₄ combustion is the focus of debate among the relevant researchers. Lu et al. conducted theoretical calculations to confirm that oxygen from PdO_x anchored at the Brønsted acid site and Pd with a low coordination number are the two key features of the active sites in methane combustion [92]. The PdO_x species anchored at the Brønsted acid center of H-ZSM-5 exhibited excellent catalytic performance and stability in CH₄ combustion. Furthermore, the $[AlO_2]Pd(OH)$ -ZSM-5 structure was the active center of CH₄ combustion. To fundamentally clarify the relationship between catalytic methane oxidation performance and the size and morphology of the wrapped Pd species, Xue and Mei used the DFT calculations combined with the first-principles thermodynamic analysis and energy span models to study the combustion of methane using different Pd species (i.e., Pd^{II}, Pd^{II}O, Pd^{II}₂O, and Pd^{II}₃O₃) encapsulated in H-SSZ-13 [121]. Under the oxidation conditions, the encapsulated $[Pd^{II}_{2}O]$ and $[Pd^{II}_{3}O_{3}]$ nanoclusters were found to be the most stable bi- and trinuclear Pd structures, whereas the encapsulated Pd^{II}₃O₃H/H-SSZ-13 nanoclusters were the most active for the combustion of CH₄, which was consistent with the previous experimental observations reported in the literature [45]. From the results of the DFT calculations and ESM model analyses, it can be realized that the reaction rate of CH_4 combustion over $Pd^{II}_{x}O_{m}H_{n}/H$ -SSZ-13 does not completely depend upon the highest activation barrier for the most kinetically relevant reaction step.

The interaction between the active species and the support and the influence of additives on the active species must be further discussed, which has an important guiding role in the development and utilization of catalysts. The essential relationship between catalyst activity and its physicochemical properties is discussed, which provides a useful basis for further improving catalytic performance and developing practical catalysts.

7. Summary and Perspectives

Zeolites provide a promising alternative to traditional metal oxides for supporting metal NPs for CH_4 combustion. Catalytic activities are related to the types of zeolites, calcination temperatures, loading methods, and the nature of noble metals. Designing a high-performance catalyst should take into consideration the following issues: (i) The zeolite-supported noble metal catalyst has good durability and recycle stability with the ideal zeolite material being hydrophobic and possessing low acidity. (ii) The zeolite-

supported noble metal catalyst has good low-temperature catalytic activity with the Pd particle sizes of 3–7 nm. Most researchers focus on the nano-composite oxide catalysts (such as metal doping, monoatomization, high-entropy alloys, and core-shell architectures) so as to create or explore the synergy between components as much as possible and improve the catalytic activities of the materials under the practical conditions. (iii) Although zeolites are promising to suppress sintering and water-induced deactivation, a major issue that cannot be ignored is that zeolite-based catalysts are highly sensitive to SO₂ poisoning. CH₄ combustion produces water, and the reaction system often contains water vapor and sulfur-containing compounds, which easily compete with CH₄ or O₂ to be adsorbed at the active sites on the catalyst surface, resulting in the decline or even deactivation of the catalyst. It is highly necessary to prevent transformation of the PdO active phase and improve SO₂ tolerance by introducing dopants, alloying, and redox active metal oxides (e.g., CeO₂).

With the worldwide consensus on reducing carbon emissions, developing energysaving industries and strictly controlling environmental problems have become the general trend and background of the world development, so the rational utilization and monitoring of methane has become a top priority. The latest progress of the complete oxidation of methane shows that zeolite-supported metal nanocatalysts bring about a great hope for the future emission control system. However, their long-term stability still has room for improvement. At the same time, it is necessary to clarify the influence mechanism of water and sulfur on a specific catalytic system in methane combustion so as to improve the anti-poisoning performance and meet the requirements for practical applications. In addition, the current laboratory-scale research lacks verification in catalytic activity and stability of the catalysts under the actual conditions, and it is difficult for laboratories to match the industrial catalytic processes. Therefore, it is also an important prerequisite for the industrial application of the monolithic catalysts to strengthen the catalytic performance and catalyst structure research under the conditions of small-scale and pilot-scale tests.

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