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Pd/Co₃O₄ 纳米颗粒负载于 Al₂O₃ 纳米片高效催化甲烷燃烧

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摘要: 我们报道了一种Pd/Co₃O₄纳米颗粒负载于Al₂O₃纳米片的三元催化剂催化甲烷的高效燃烧。其中, Pd/Co₃O₄负载于碱性氧化铝的复合材料活化甲烷C—H键的能力比SiO₂、ZrO₂和CeO₂以及酸性和中性Al₂O₃为载体时更强, 这是因为Pd/Co₃O₄/碱性Al₂O₃拥有更多的氧空穴和吸附氧, 对催化剂催化甲烷燃烧有较好的影响。尽管在5%(体积分数)的水蒸气存在下, 其催化性能有一定的失活, 但在移除水蒸气时, 其催化性能可以快速恢复至最佳状态。在模拟真实汽车尾气的氛围下, Pd/Co₃O₄/碱性Al₂O₃依然具有较好的催化甲烷燃烧性能, 在400 °C时可以催化甲烷完全转化。

关键词: Pd/Co₃O₄; 碱性; 甲烷氧化; 活性; 稳定性

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Pd/Co₃O₄ Nanoparticles Inlaid in Alkaline Al₂O₃ Nanosheets as an Efficient Catalyst for Catalytic Oxidation of Methane

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Abstract: We report an efficient catalyst composed of ternary components prepared by inlaying Pd/Co₃O₄ nanoparticles in alkaline Al₂O₃ nanosheets for catalytic oxidation of methane. Pd/Co₃O₄ inlaid in alkaline Al₂O₃ exhibited a higher ability to break the C—H bond of methane than Pd/Co₃O₄ supported on SiO₂, ZrO₂, CeO₂, and acidic or neutral Al₂O₃. Our results show more oxygen vacancies and higher amounts of surface adsorbed oxygen on the surface of Pd/Co₃O₄/alkaline Al₂O₃ than on other catalysts, which is responsible for methane activation and conversion. Further, the Pd/Co₃O₄/alkaline Al₂O₃ catalyst can almost restore to its initial value in the absence of water when 5% (volume fraction) vapor water was cut off, although a decrease in activity occurred when water vapor was introduced to the reaction system. Even under a condition similar to the exhaust of a lean-burn natural gas engine, the catalytic performance of the Pd/Co₃O₄/alkaline Al₂O₃ catalyst is excellent, that is, methane could be completely converted when the sample temperature in the reaction atmosphere was ramped to 400 °C.

Key Words: Pd/Co₃O₄; Alkaline Al₂O₃; Methane oxidation; Activity; Stability

1 Introduction

Natural gas, of which methane is the major component, is widely used in power generation, vehicle fuel and other heating

applications¹. Methane is a very stable and symmetrical molecule containing four C—H bonds². The breaking of the C—H bond is thermodynamically unfavorable and the energy

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of methane activation is higher than those of higher hydrocarbons³. Therefore, the conversion of methane, such as oxidative coupling of methane for ethane and ethylene⁴, methane dry reforming for CO and H₂⁵, and partial oxidation of methane for methanol⁶, need carrying out at high temperature even if in the presence of catalysts. The catalytic combustion of methane, as one of methane conversion, cannot be happened at low temperature and the complete methane combustion is obtained below at least 400 °C in the very active catalysts⁷⁻⁹. However, the complete oxidation of unburned methane from exhaust streams is significant for that the greenhouse effect of methane is more than 20 times than that of carbon dioxide, and the incomplete oxidation could bring about various nitrogen oxides, carbon monoxide, and soot emissions¹⁰. With given more attention to environment and health, the high catalytically active and stable catalysts thus are highly desirable to, in principle, emission limit of methane to the atmosphere, and simultaneously reduce NO_x, CO and soot emissions to ultra-low levels¹¹. Current popular catalysts for methane catalytic combustion are noble metals and metal oxides^{12,13}. Several crucial factors need to be considered in developing new catalysts for catalytic combustion of methane, such as high sintering rates, high cost of noble metals, water and sulfur poisoning^{14,15}. Palladium-based catalysts are known as the very effective catalysts for catalytic methane oxidation, and unfortunately, they tend to deactivate because of sintering at high temperature^{14,16}. Other catalysts based on oxides such as transition metal oxides, perovskite oxides and hexaaluminate oxides show low catalytic activity, with the complete conversion of methane observed only above 400 °C¹⁷⁻¹⁹.

In terms of Pd-based catalysts, many efforts have been made to investigate the influence of the metal-oxide support on the activity and the stability of the palladium catalyst, the impact of the support is mainly credited to palladium dispersion, oxygen mobility, and the Pd-support interaction^{20,21}. The metal oxides not only work as supports but also function as electronic modulators to contribution spillover and adsorption sites^{22,23}. Co₃O₄ with typical spinel-structure transition metal oxide is an important support for Pd-based catalysts in the activation of methane, since there is a strong interaction between the Co₃O₄ unit cell and the PdO unit cell^{24,25}. Aluminum oxides (especially γ -Al₂O₃), with high surface area, moderate chemical activity, and low cost, are also widely employed as supports for methane combustion^{26,27}.

In view of the virtue of Co₃O₄ and Al₂O₃ as supports, herein, we produce an efficient catalyst such Pd/Co₃O₄/Al₂O₃ through inlaying Pd/Co₃O₄ nanoparticles in Al₂O₃ nanosheets for catalytic oxidation of methane. Pd/Co₃O₄ inlaid in Al₂O₃ catalysts exhibit higher catalytic ability compared to SiO₂, ZrO₂ and CeO₂ as supports. Pd/Co₃O₄ supported on alkaline Al₂O₃ nanosheets is more efficient than Pd/Co₃O₄ supported on acidic or neutral Al₂O₃ for methane oxidation. Finally, Pd/Co₃O₄/alkaline Al₂O₃ catalyst exhibited superior

performance for methane oxidation in the presence of water vapor and a mixed gas similar to the exhaust of lean-burn natural gas engine, which indicates that this catalyst would be very interesting for this application.

2 Experimental

2.1 Chemicals and reagents

Cobalt (II) acetate tetrahydrate (Co(Ac)₂·4H₂O, 99.5%), ethylene glycol (EG, 99%), sodium carbonate anhydrous (Na₂CO₃, 99.8%), and potassium tetrachloropalladate (K₂PdCl₄, 98%), were purchased from Aladdin reagent Co., Ltd. Acidic Al₂O₃ (FCP, 200–300 mesh), neutral Al₂O₃ (FCP, 200–300 mesh), alkaline Al₂O₃ (FCP, 200–300 mesh) (the acid-base property of these Al₂O₃ explained by the CO₂ temperature-program desorption was shown in Fig.S1 (Supporting Information)), SiO₂ (AR), ZrO₂ (AR), CeO₂ (AR), were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the chemicals were used directly without further treatment except metal oxides. Metal oxides were pretreated at 900 °C for 12 h.

2.2 Catalysts preparation

Pd/Co₃O₄ nanoparticles: Co(Ac)₂·4H₂O (5 mmol) was dissolved in ethylene glycol (15 mL) at 80 °C under vigorous stirring and argon flow. Na₂CO₃ aqueous solution (0.2 mol·L⁻¹, 50 mL) was then added to the mixture drop-wisely and purple precipitate was gained, which was further aged for 10 min at 80 °C. After that, to maintain the metal loading on the Co₃O₄ supported catalysts, 10 mL aqueous solution of appropriate amount of Na₂PdCl₄ was then added to the aforementioned solution. The resulting solution was further aged at that temperature for 1.5 h. After the solution was cooled to room temperature, a dark purple solid precipitate was separated by centrifugation with successive repeated washing with water and ethanol. After the precipitate was dried at 60 °C in vacuum, the obtained Pd/cobalt hydroxycarbonate was calcined to produce Pd/Co₃O₄ nanoparticles in air at 300 °C for 3 h.

Pd/Co₃O₄ and Al₂O₃ (or SiO₂, ZrO₂, CeO₂) were co-added into 15 mL of ethanol and the mixture stirred overnight. Solvent was then centrifugation and the powder dried at 120 °C overnight, ground to a particle size below 150 μ m and calcined in air at 500 °C for 5 h.

2.3 Catalysts characterization

Powder X-ray diffraction (XRD) of the samples was recorded on an Ultima IV, made in Japan, performed with Cu K α radiation (0.15418 nm). The TEM image, HAADF and element mapping images were acquired from using the transmission electron microscope (G2 F20 S-Twin, FEI, America) equipped with energy dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 200 kV. The binding energies of surface species on the catalysts were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, America) using Al K α ($h\nu$ = 1486.6 eV) as the excitation source and the pass energy is 145 eV. The N₂

sorption experiments were done with physical adsorption analyzer (TriStar II 3020, Micromeritics, Germany). All the samples were degassed at 200 °C for 6 h under vacuum prior to measurement. The surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. Methane temperature-programmed reduction (CH₄-TPR) and oxygen temperature-programmed desorption (O₂-TPD) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, America) with a mass spectrograph (Cirrus 2). Before TPR measurement, 50 mg of catalyst was pretreated in an air flow at 300 °C for 2 h. After being cooled at the same atmosphere to 60 °C, the sample was exposed to a flow (50 mL·min⁻¹) of 10% (volume fraction) CH₄ 90% (volume fraction) He mixture and kept at 60 °C for 1 h, finally the pretreated sample was heated from 60 to 800 °C at a ramp of 10 °C·min⁻¹; and before TPD measurement, 200 mg of catalyst was pretreated in an He flow at 300 °C for 2 h. After being cooled at the same atmosphere to 60 °C, the sample was exposed to a flow (50 mL·min⁻¹) of 1% (volume fraction) O₂ 99% (volume fraction) He mixture and kept at 60 °C for 2 h, and then turned to a He flow for 2 h, finally the pretreated sample was heated from 60 to 800 °C at a ramp of 10 °C·min⁻¹.

2.4 Catalytic evaluation

Catalytic combustion of methane was measured using a conventional quartz tubular reactor (diameter, 6 mm; length, 500 mm) at atmospheric pressure. The reagent gas mixture (1% (volume fraction) CH₄, 10% (volume fraction) O₂ and 89% (volume fraction) N₂) was led over catalysts (40–60 mesh, 0.1 g) at a flow rate of 100 mL·min⁻¹, equivalent to a space velocity (SV) of 30000 mL·g⁻¹·h⁻¹. The reaction of methane combustion was heated from 20 to 450 °C at a ramp of 5 °C·min⁻¹. The reaction products were analyzed by micro gas chromatograph (INFICON 3000) equipped with MSSA and Plot Q columns (for separation of H₂, CO, N₂, CO₂, O₂, CH₄, C₂H₄, and C₂H₆) and TCD detector.

3 Results and discussion

Catalytic performance toward methane oxidation was evaluated by obtaining methane conversion vs temperature profiles of Pd/Co₃O₄ nanoparticles loaded on different oxide supports (0.6% (mass fraction) Pd and 9.4% (mass fraction) Co₃O₄ supported on alkaline Al₂O₃ (denoted as al-Al₂O₃), SiO₂, ZrO₂ or CeO₂, respectively) for comparison. All the catalysts showed 100% selectivity toward CO₂, and no CO was observed during the reaction. Pd/Co₃O₄/al-Al₂O₃ catalyst is more effective than other three catalysts for methane oxidation. As shown in Fig.1A, methane can be lighted off at 250 °C and completely oxidized at 400 °C over Pd/Co₃O₄/al-Al₂O₃ catalyst at a flow rate of 100 mL·min⁻¹ with 1% (volume fraction) CH₄ and 10% (volume fraction) O₂ balanced with N₂. Although methane can be ignited over Pd/Co₃O₄/SiO₂ catalyst at 250 °C, the complete oxidation of methane cannot be obtained at 400 °C, that is, only 70% methane was oxidized at 400 °C.

Methane needs higher energy to be activated and converted over Pd/Co₃O₄/ZrO₂ and Pd/Co₃O₄/CeO₂ catalysts, where methane was initially activated at above 275 °C and less than 90% methane was converted at 400 °C. The kinetics of methane oxidation at the initial stages of reaction was studied, and a good linear relation with data reveals the pseudo first-order model of methane. It is noted that the reaction rate of Pd/Co₃O₄/SiO₂ catalyst is faster than other ones at a low operating temperature (< 325 °C), while the conversion of methane over Pd/Co₃O₄/al-Al₂O₃ catalyst is the highest among the four catalysts at above 325 °C (Fig.1B).

Afterwards, we studied the influence of acidic, neutral and alkaline properties of Al₂O₃ substrate on the catalytic behavior of Pd/Co₃O₄ for catalytic oxidation of methane. From Fig.1C, Pd/Co₃O₄/acidic Al₂O₃ and Pd/Co₃O₄/neutral Al₂O₃ catalysts did not give the complete oxidation of methane at 425 °C. T_{90} of the two catalysts are 40 °C higher than the case of Pd/Co₃O₄/alkaline Al₂O₃. The measured T_{10} and T_{90} temperatures follow the order of Pd/Co₃O₄/alkaline Al₂O₃ < Pd/Co₃O₄/acidic Al₂O₃ ≈ Pd/Co₃O₄/neutral Al₂O₃. It can be observed from Table 1 that the apparent activation energy increased in the sequence Pd/Co₃O₄/alkaline Al₂O₃ < Pd/Co₃O₄/acidic Al₂O₃ < Pd/Co₃O₄/neutral Al₂O₃, with the lowest E_a value (134 kJ·mol⁻¹) being achieved over the Pd/Co₃O₄/alkaline Al₂O₃. It indicates that methane oxidation proceed more readily over Pd/Co₃O₄/alkaline Al₂O₃.

The high efficient activity of Pd/Co₃O₄/al-Al₂O₃ catalyst is partially associated with its strong redox property, which has been confirmed by the CH₄ temperature-program reduction studies. The CH₄-TPR results are shown in Fig.2, and the consumption peaks of CH₄ and the formation of CO₂, H₂O, CO, and H₂ are detected. For Pd/Co₃O₄/al-Al₂O₃ in Fig.2A, the first consumption peak of CH₄ at 232 °C is attributed to the reduction process of the PdO_x with CH₄ toward Pd⁰. The second one at 420 °C is related with the reduction reaction of Co₃O₄ with CH₄ from Co³⁺ to Co²⁺. The third consumption peak at 525 °C corresponds to the reduction process of Co₃O₄ with CH₄ from Co²⁺ to Co⁰ and the reforming reaction of CH₄ and CO₂ or H₂O under the catalysis of Co⁰ or Pd⁰ species, due to the formation of CO₂, H₂O, CO and H₂²⁸. The fourth weak peak centered 537 °C can be attributed to the cracking of CH₄. For the Pd/Co₃O₄/SiO₂ in Fig.2B, the reduction peak of Pd^{δ+} to Pd⁰ shifts to 281 °C and the reduction peak of Co³⁺ to Co²⁺ moves to 313 °C, respectively. The peak at 706 °C with the formation of H₂O and trace CO₂ and CO might result from the reduction of Co²⁺ to Co⁰. In terms of Pd/Co₃O₄/ZrO₂ in Fig.2C, the peaks of Pd^{δ+} to Pd⁰ and Co³⁺ to Co²⁺ move to 304 and 381 °C, and the peak at 393 °C is attributed to the reduction of Co²⁺ to Co⁰ and the reforming of methane. The peak at 669 °C is assigned to the cracking of methane. As to Pd/Co₃O₄/CeO₂ shown in Fig.2D, the four peaks are observed at 290, 415, 578 and 676 °C, respectively, due to the reduction of Pd^{δ+} to Pd⁰, Co³⁺ and Co²⁺ to Co⁰, cracking of methane, and the reforming

Fig.1 (A) The catalytic performance and (B) the corresponding kinetic rate data of Pd/Co₃O₄ nanoparticles supported on (a) alkaline Al₂O₃, (b) SiO₂, (c) ZrO₂ and (d) CeO₂ for catalytic oxidation of methane, respectively; (C) the light-off profiles of catalytic oxidation of methane over (e) Pd/Co₃O₄/acidic Al₂O₃ (denoted as ac-Al₂O₃), (f) Pd/Co₃O₄/neutral Al₂O₃ (denoted as ne-Al₂O₃), and (a) Pd/Co₃O₄/alkaline Al₂O₃, respectively, (D) the corresponding kinetic rate data for methane oxidation.

of methane. According to reduction temperatures, the redox ability of the catalysts are followed a descended sequence: Pd/Co₃O₄/al-Al₂O₃ < Pd/Co₃O₄/SiO₂ < Pd/Co₃O₄/CeO₂ < Pd/Co₃O₄/ZrO₂, which is basically in consistent with the activity sequence of the catalysts except Pd/Co₃O₄/SiO₂. From the CH₄-TPR studies, as shown in Fig.2(E-F), the peak of Pd^{δ+} to Pd⁰, the peak of Co³⁺ to Co²⁺ and the peak of Co²⁺ to Co⁰ shift toward the higher temperatures. This result illustrates that Pd-Co₃O₄/alkaline Al₂O₃ has more oxygen vacancies on the surface as compared to other two catalysts such as Pd/Co₃O₄/acidic Al₂O₃ and Pd/Co₃O₄/neutral Al₂O₃, since it is easier to generate oxygen vacancies for Pd/Co₃O₄/al-Al₂O₃ catalyst that is more susceptible reducible. Thus a collective

contribution from more reactive oxygen species and stronger redox ability contributes to the higher activity of Pd/Co₃O₄/al-Al₂O₃ catalyst.

As we known, the adsorbed oxygen species are more active than the lattice oxygen for catalytic oxidation of methane. The more effective activity of alkaline Al₂O₃ loaded by Pd/Co₃O₄ for methane oxidation is also attributed to the more adsorbed oxygen species of this catalyst. From the analysis of O₂-TPD data shown in Fig.3, the peaks below 400 °C are attributed to the desorption of surface adsorbed oxygen species (such as O₂⁻ and O⁻), while the peaks beyond 700 °C are assigned to the desorption of lattice oxygen species. The abroad band of Pd/Co₃O₄/alkaline Al₂O₃ at about 200–400 °C points out the

Table 1 BET specific surface area (S_{BET}) from N₂ absorption isotherms, the molar ratios of adsorbed oxygen/lattice oxygen ($O_{\text{ads}}/O_{\text{latt}}$), Pd^{δ+}/Pd⁰, and Co²⁺/Co³⁺ detected from XPS, the temperatures for 10%, 50% and 90% conversion of methane (T_{10} , T_{50} and T_{90}), and apparent activation energy (E_a).

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$O_{\text{ads}}/O_{\text{latt}}$	Pd ^{δ+} /Pd ⁰	Co ²⁺ /Co ³⁺	$T_{10}/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_{90}/^\circ\text{C}$	$E_a/(\text{kJ} \cdot \text{mol}^{-1})$
0.6Pd/9.4Co ₃ O ₄ /al-Al ₂ O ₃	33	0.45	32	1.2	291	340	374	134
0.6Pd/9.4Co ₃ O ₄ /SiO ₂	13	0.50	18	1.0	282	358	434	92
0.6Pd/9.4Co ₃ O ₄ /ZrO ₂	27	0.23	-	0.7	315	375	405	198
0.6Pd/9.4Co ₃ O ₄ /CeO ₂	31	0.26	64	0.6	296	369	407	194
0.6Pd/9.4Co ₃ O ₄ /ac-Al ₂ O ₃	29	1.64	39	0.7	316	370	415	149
0.6Pd/9.4Co ₃ O ₄ /ne-Al ₂ O ₃	31	1.91	13	0.6	312	371	417	153

Fig.2 CH₄ temperature-program reduction spectra of (A) Pd/Co₃O₄/alkaline Al₂O₃, (B) Pd/Co₃O₄/SiO₂, (C) Pd/Co₃O₄/ZrO₂, (D) Pd/Co₃O₄/CeO₂, (E) Pd/Co₃O₄/acidic Al₂O₃, and (F) Pd/Co₃O₄/neutral Al₂O₃.

Fig.3 O₂ temperature-program desorption spectra of (a) Pd/Co₃O₄/alkaline Al₂O₃, (b) Pd/Co₃O₄/SiO₂, (c) Pd/Co₃O₄/ZrO₂, (d) Pd/Co₃O₄/CeO₂, (e) Pd/Co₃O₄/acidic Al₂O₃, and (f) Pd/Co₃O₄/neutral Al₂O₃.

presence of reactive oxygen species on the surface of this catalyst, while no obvious signal of adsorbed oxygen species were found on other five catalysts, indicating that alkaline Al₂O₃ benefits for the formation of adsorbed oxygen species, which ultimately promotes the activation of methane on Pd/Co₃O₄/alkaline Al₂O₃ catalyst.

Besides the comparison of the redox property and active oxygen species of the catalysts, we now turn to consider the surface compositions, which were showed in Fig.S2 and Table S1. Pd 3d binding energy^{29,30} of the five samples except Pd/Co₃O₄/ZrO₂ (note: Pd peaks are overlapped by Zr peaks) show no shift toward high or low binding energy and the cationic Pd^{δ+} dominates the surface of samples, as shown in Fig.4A, while the presence of trace Pd⁰ is in Pd 3d spectra of the five samples. The molar ratios of Pd^{δ+}/Pd⁰ of these samples were calculated and listed in Table 1. Here the ratio value of Pd^{δ+}/Pd⁰ seems to be not directly related with the catalytic activity, though PdO is more active than Pd for methane

oxidation. Fig.4B presents the Co 2p spectra and it is found that the occurrence of satellite structure leads to the deconvolution of Co 2p_{1/2} and 2p_{3/2} excitations. The peaks located at 781.8 eV are attributable to Co²⁺, and the peaks at 779.9 eV are assigned to Co³⁺^{29,31,32}, which revealed the presence of Co²⁺ and Co³⁺ of all samples, demonstrating that CoO and Co₂O₃ dominated the surface of the samples. The molar ratios of Co²⁺/Co³⁺ listed in Table 1 indicated that Pd/Co₃O₄/al-Al₂O₃ gave the highest value of Co²⁺/Co³⁺ among these samples. Co²⁺ is considered to be the source of oxygen vacancy and raising the relative amount of Co²⁺ on the catalysts' surface benefits for increasing the amount of oxygen vacancy and then benefits for methane conversion^{7,13}. Thus the high concentration of Co²⁺ might be one reason to explain the high activity of Pd/Co₃O₄/al-Al₂O₃. However, the detailed order for Co²⁺/Co³⁺ value of these catalysts follows Pd/Co₃O₄/al-Al₂O₃ > Pd/Co₃O₄/SiO₂ > Pd/Co₃O₄/ZrO₂ > Pd/Co₃O₄/CeO₂, and Pd/Co₃O₄/al-Al₂O₃ > Pd/Co₃O₄/acidic Al₂O₃ > Pd/Co₃O₄/neutral Al₂O₃, which is

Fig.4 (A) Pd 3d and (B) Co 2p of (a) Pd/Co₃O₄/alkaline Al₂O₃, (b) Pd/Co₃O₄/SiO₂, (c) Pd/Co₃O₄/ZrO₂, (d) Pd/Co₃O₄/CeO₂, (e) Pd/Co₃O₄/acidic Al₂O₃, and (f) Pd/Co₃O₄/neutral Al₂O₃.

Fig.5 (A) Nitrogen adsorption-desorption isotherms of (a) Pd/Co₃O₄/alkaline Al₂O₃, (b) Pd/Co₃O₄/SiO₂, (c) Pd/Co₃O₄/ZrO₂, (d) Pd/Co₃O₄/CeO₂, (e) Pd/Co₃O₄/acidic Al₂O₃, and (f) Pd/Co₃O₄/neutral Al₂O₃; (B) the corresponding pore size distribution.

almost but no complete agreement with the experimental results obtained in methane oxidation. Actually, the activity is attributed to the collective contribution from all factors rather than only one.

The BET surface areas and pore characters of these catalysts were determined from N₂ sorption measurements, which are shown in Fig.5 and Table 1. The BET surface area of these six catalysts (except SiO₂) seems to be very close, suggesting that their catalytic activity seems to be not directly related with their specific surface area.

We also investigated the effect of loading amount of Pd and Co₃O₄ on alkaline Al₂O₃ on the catalytic performance of methane oxidation. When the loading amount of Pd/Co₃O₄ is fixed to 10% (mass fraction), it is found that as the amount of Pd loaded on Co₃O₄ is turned into 3% (mass fraction), 5% (mass fraction), 6% (mass fraction) and 10% (mass fraction), respectively, a interesting phenomenon is observed that 0.6Pd/9.4Co₃O₄/Al₂O₃ (the loading amount of Pd is 6% (mass fraction)) catalyst showed superior catalytic performance (Fig.6A) to 0.3Pd/9.7Co₃O₄/Al₂O₃, 0.5Pd/9.5Co₃O₄/Al₂O₃ and 1.0Pd/9.0Co₃O₄/Al₂O₃. As shown in Fig.6B, when the amount of Pd loaded on Co₃O₄ is fixed to 5% (mass fraction),

0.75Pd/14.25Co₃O₄/Al₂O₃ (15% Pd/Co₃O₄ on Al₂O₃) and 1.0Pd/19.0Co₃O₄/Al₂O₃ (20% Pd/Co₃O₄ on Al₂O₃) are similar light-off curves of catalytic oxidation of methane, yet which are higher activity than 0.5Pd/9.5Co₃O₄/Al₂O₃ (10% Pd/Co₃O₄ on Al₂O₃) catalyst. When the amount of Pd loaded on Co₃O₄ is fixed to 6% (mass fraction), for the three catalysts, such as 0.9Pd/14.1Co₃O₄/Al₂O₃ (15% (mass fraction) Pd/Co₃O₄ on Al₂O₃) and 1.2Pd/18.8Co₃O₄/Al₂O₃ (20% (mass fraction) Pd/Co₃O₄ on Al₂O₃), the temperatures of methane conversion are close over the two catalysts under same evaluation condition, which is lower than that of 0.6Pd/9.4Co₃O₄/Al₂O₃ 10% (mass fraction) Pd/Co₃O₄ on Al₂O₃) (Fig.6B). Thus, from the above results, even if the weight percent of Pd is above 0.6%, 0.6Pd/9.4Co₃O₄/al-Al₂O₃ always gave the highest catalytic activity among these catalysts.

Hence 0.6Pd/9.4Co₃O₄/al-Al₂O₃ catalyst holds promising in its utility as a type of Pd-based catalysts that offer high activity for methane oxidation. Especially, this catalyst displayed a long-term stability without an obvious decline in activity whatever cycles and time-on-stream experiments. When the temperature was ramped from 250 to 400 °C and then cooled back to 250 °C, the light off curve for upward ramp was

Fig.6 (A, B) Catalytic results of methane oxidation over Pd/Co₃O₄/al-Al₂O₃ with different loading amount of Pd and Co₃O₄; (C) cycle of heating and cooling cycle profiles of methane conversion against the temperature for 0.6Pd/9.4Co₃O₄/al-Al₂O₃; (D) catalytic stability of 0.6Pd/9.4Co₃O₄/al-Al₂O₃ at 380 °C for 50 h (the upper panel), and 500 °C for 50 h (the lower panel); (E) 5% (volume fraction) vapor water effect on the catalytic performance of 0.6Pd/9.4Co₃O₄/al-Al₂O₃ at 380 °C.

(a) 0.3Pd/9.7Co₃O₄/al-Al₂O₃, (b) 0.5Pd/9.5Co₃O₄/al-Al₂O₃, (c) 0.6Pd/9.4Co₃O₄/al-Al₂O₃, (d) 1.0Pd/9.0Co₃O₄/al-Al₂O₃,
(e) 0.45Pd/14.55Co₃O₄/al-Al₂O₃, (f) 0.6Pd/19.4Co₃O₄/al-Al₂O₃, (g) 0.5Pd/9.5Co₃O₄/al-Al₂O₃, (h) 0.75Pd/14.25Co₃O₄/al-Al₂O₃,
(i) 1.0Pd/19.0Co₃O₄/al-Al₂O₃, (j) 0.9Pd/14.1Co₃O₄/al-Al₂O₃, (k) 1.2Pd/18.8Co₃O₄/al-Al₂O₃.

virtually identical to one for downward ramp (Fig.6C). The second heating and cooling cycle test showed no significant deactivation compared to the first cycle (Fig.6C). Moreover, 0.6Pd/9.4Co₃O₄/al-Al₂O₃ catalyst exhibited a high sintering resistance at high temperature. When the temperature was kept at 380 °C, noted that the conversion of methane is not complete, the conversion of methane can always be maintained about 97% for at least 50 hours (the upper panel of Fig.6D). Even if the temperature was fixed at high temperature such 500 °C, the 100% conversion of methane over 0.6Pd/9.4Co₃O₄/al-Al₂O₃ can be obtained when the reaction time was up to 50 hours (the lower panel of Fig.6D). Especially, the effect of moisture on the catalytic performance of this catalyst for methane oxidation was examined. To investigate the catalytic performance of the catalysts for wet methane combustion, 5% (volume fraction) of water vapor was introduced by a calibrated water pump and vaporized in the heated gas feed line before entering the reactor. It is found that Pd/Co₃O₄/alkaline Al₂O₃ catalyst can almost restore to its initial value in the absence of water when 5% (volume fraction) water was cut off and the reaction temperature was at 380 °C,

although a decrease from 97% to 80% in activity occurred when water was introduced to the reaction system (Fig.6E).

Interestingly, the structure of Pd/Co₃O₄/al-Al₂O₃ catalyst has very little change and no significant aggregation after catalytic reaction when compared to the fresh one (Fig.7). For fresh catalyst with the average PdO particle size of 6 nm, we can see the (220) and (222) lattice fringe with interplanar spacing of 0.199 and 0.163 nm (calculated from the fast Fourier transformed pattern of the red circled area shown in Fig.7B and 7E) on the PdO (Fig.7B). The lattice spacing of 0.232 nm can be assigned to the (111) lattice fringe of Co₃O₄. The energy-dispersive X-ray spectroscopy (EDS) mapping analysis (Fig.7C) clearly points to the distribution ranges of Pd (red) and Co (blue) in the nanoparticle, revealing the homogenous distribution of Pd and Co in Al₂O₃ support. After catalytic test, TEM studies offer further insight into the structural information of spent catalyst. For spent catalyst with the average PdO particle size of 10 nm in Fig.7(D-F), Pd and Co are coexisted on the support and the contact of PdO and Co₃O₄ is still intimate, which indeed ensures a high resistance to sintering of active sites at thermal condition.

Fig.7 (A) TEM and (B) HRTEM images (inset: the fast Fourier transformed pattern of the red circled area, spots 1, 2 and 3 represent the Co_3O_4 (111), PdO (220) and PdO (222), respectively) of fresh 0.6Pd/9.4 Co_3O_4 /al- Al_2O_3 catalyst and (C) corresponding EDS elemental mapping. (D) TEM and (E) HRTEM images (inset: the fast Fourier transformed pattern of the red circled area, spots 1, 2 and 3 represent the Co_3O_4 (111), PdO (220) and PdO (220), respectively) of spent 0.6Pd/9.4 Co_3O_4 /al- Al_2O_3 catalyst and (F) corresponding EDS elemental mapping.

Fig.8 Catalytic performance of 0.6Pd/9.4 Co_3O_4 /al- Al_2O_3 under conditions simulating the mixture gases of exhaust of engines of natural gas vehicles.

(Gas A) gas composition, CH_4 : 0.20%, O_2 : 10%, CO_2 : 15%, H_2O : 5%, N_2 : 69.8%;

(Gas B) gas composition, CH_4 : 0.20%, O_2 : 10%, NO : 0.15%, H_2O : 5%, N_2 : 84.65%.

Further, to evaluate the catalytic performance of 0.6Pd/9.4 Co_3O_4 /al- Al_2O_3 catalyst in methane oxidation of gas exhaust of an engine of natural gas, two different mixed gases similar to the exhaust of lean-burn natural gas engine were used³²: one is composed with CH_4 : 0.20%, O_2 : 10%, CO_2 : 15%, H_2O : 5% and N_2 as the balance at space velocity of 30000 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, and the other is mixed with CH_4 : 0.20%, O_2 : 10%, NO : 0.15%, H_2O : 5% balanced with N_2 . In the case of CH_4 : 0.20%, O_2 : 10%, CO_2 : 15%, H_2O : 5%, and N_2 : 69.80%, 0.6Pd/9.4 Co_3O_4 /al- Al_2O_3 catalyst gave rise to a complete conversion of methane at 400 °C. From Fig.8, in the mixture of CH_4 : 0.20%, O_2 : 10%, NO : 0.15%, H_2O : 5%, and N_2 : 84.65%, 100% conversion of methane can be achieved over 0.6Pd/9.4 Co_3O_4 /al- Al_2O_3 catalyst at 425 °C. The results reflect

that Pd/ Co_3O_4 / Al_2O_3 catalyst shows higher activity than Pd/ Al_2O_3 reported above 500 °C under the conditions simulating the typical gas composition of the exhaust of engines of natural gas³³.

4 Conclusions

In summary, we report an efficient catalyst composed of ternary components via Pd/ Co_3O_4 nanoparticles inlaid in alkaline Al_2O_3 nanosheets for catalytic oxidation of methane. The high adsorbed oxygen species concentration and strong redox properties appear to enhance the oxidation activity of Pd/ Co_3O_4 /al- Al_2O_3 . The intimate contact of Pd/ Co_3O_4 with Al_2O_3 ensures a high resistance toward sintering at thermal condition. The addition of 5% (volume fraction) water did not seriously affect the catalytic activity of Pd/ Co_3O_4 /al- Al_2O_3 and the activity can restore to its initial value in the absence of water when the water was cut off. The excellent catalytic behavior for methane oxidation of Pd/ Co_3O_4 /al- Al_2O_3 highlights the importance of pursuing the ternary recipes for real-world application.

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Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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Pd/Co₃O₄ 纳米颗粒负载于 Al₂O₃ 纳米片高效催化甲烷燃烧

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Pd/Co₃O₄ Nanoparticles Inlaid in Alkaline Al₂O₃ Nanosheets as an Efficient Catalyst for Catalytic Oxidation of Methane

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The acid-base property of these Al_2O_3 is explained by the CO_2 temperature-program desorption, which is shown in Fig.S1. The detailed order of the CO_2 desorption peaks' temperature follows the sequence of $\text{al-Al}_2\text{O}_3 > \text{ne-Al}_2\text{O}_3 > \text{ac-Al}_2\text{O}_3$, infirming that the alkalinity order of these Al_2O_3 follows $\text{al-Al}_2\text{O}_3 > \text{ne-Al}_2\text{O}_3 > \text{ac-Al}_2\text{O}_3$.

Fig.S1 CO_2 temperature-program desorption spectra of $\text{al-Al}_2\text{O}_3$, $\text{ac-Al}_2\text{O}_3$, and $\text{ne-Al}_2\text{O}_3$.

The surface concentration information of these examined catalysts are shown in Fig.S2 and listed in the Table S1 below, showing that the examined catalysts have no residual alkali metals, indicating that Na was removed in the washing and centrifugation process.

Fig.S2 The survey spectra of (a) $\text{Pd/Co}_3\text{O}_4/\text{alkaline Al}_2\text{O}_3$, (b) $\text{Pd/Co}_3\text{O}_4/\text{SiO}_2$, (c) $\text{Pd/Co}_3\text{O}_4/\text{ZrO}_2$, (d) $\text{Pd/Co}_3\text{O}_4/\text{CeO}_2$, (e) $\text{Pd/Co}_3\text{O}_4/\text{acidic Al}_2\text{O}_3$, and (f) $\text{Pd/Co}_3\text{O}_4/\text{neutral Al}_2\text{O}_3$.

Table S1 The surface composition of (a) Pd/Co₃O₄/alkaline Al₂O₃, (b) Pd/Co₃O₄/SiO₂, (c) Pd/Co₃O₄/ZrO₂, (d) Pd/Co₃O₄/CeO₂, (e) Pd/Co₃O₄/acidic Al₂O₃, and (f) Pd/Co₃O₄/neutral Al₂O₃.

Sample	Al/Si /Zr/Ce	C	O	Pd	Co
0.6Pd/9.4Co ₃ O ₄ /al-Al ₂ O ₃	30.4	21.4	45.5	0.2	2.6
0.6Pd/9.4Co ₃ O ₄ /SiO ₂	34.8	4.4	58.3	0.1	2.4
0.6Pd/9.4Co ₃ O ₄ /ZrO ₂	22.2	28.8	43.7	-	3.7
0.6Pd/9.4Co ₃ O ₄ /CeO ₂	10.7	35.8	48.2	0.6	4.6
0.6Pd/9.4Co ₃ O ₄ /ac-Al ₂ O ₃	17.6	39.0	38.4	0.3	4.8
0.6Pd/9.4Co ₃ O ₄ /ne-Al ₂ O ₃	21.1	33.7	41.7	0.2	3.3

Table S2 The actual Pd content of the catalysts.

Sample	Pd content/%
0.6Pd/9.4Co ₃ O ₄ /al-Al ₂ O ₃	0.57
0.6Pd/9.4Co ₃ O ₄ /SiO ₂	0.56
0.6Pd/9.4Co ₃ O ₄ /ZrO ₂	0.59
0.6Pd/9.4Co ₃ O ₄ /CeO ₂	0.60
0.6Pd/9.4Co ₃ O ₄ /ac-Al ₂ O ₃	0.58
0.6Pd/9.4Co ₃ O ₄ /ne-Al ₂ O ₃	0.61