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Influence of NO_x on the activity of Pd/ θ -Al₂O₃ catalyst for methane oxidation: Alleviation of transient deactivation

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ABSTRACT

Alumina supported Pd catalyst (Pd/Al₂O₃) is active for complete oxidation of methane, while often suffers transient deactivation during the cold down process. Herein, heating and cooling cycle tests between 200 and 900°C and isothermal experiments at 650°C were conducted to investigate the influence of NO_x on transient deactivation of Pd/ θ -Al₂O₃ catalyst during the methane oxidation. It was found that the co-fed of NO alleviated transient deactivation in the cooling ramp from 800 to 500°C, which was resulted from the in situ formation of NO₂ during the process of methane oxidation. Over the Pd/θ -Al₂O₃, thermogravimetric analysis and O2 temperature programmed oxidation measurements confirmed that transient deactivation was due to the decomposition of PdO particles and the hysteresis of Pd reoxidation, while the metal Pd entities were less active for methane oxidation than the PdO ones. CO pulse chemisorption and scanning transmission electron microscopy characterizations rule out the NO₂ effect on Pd size change. Powder X-ray diffraction and X-ray photoelectron spectroscopy characterizations were used to obtain palladium status of Pd/θ -Al₂O₃ before and after reactions, indicating that in lean conditions at 650°C, the presence of NO2 increases the content of active PdO on the catalyst surface, thus benefits methane oxidation. Homogeneous reaction between CH₄, O₂, and NO_x may be partially responsible for the alleviation above 650°C. The interesting research of alleviation in transient deactivation by NO_x, the components co-existing in exhausts, are of great significance for the application.

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Introduction

Natural gas vehicles (NGVs) are widely developed as substitutes for gasoline and diesel vehicles, due to lower price and less pollutants emissions (Engerer and Horn, 2010;

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Huang et al., 2020; Wang et al., 2014). In this field, leanburn engines have lower emissions of total hydrocarbons and better fuel economy than stoichiometric operation ones (Karavalakis et al., 2016). As for lean-burn natural gas engines, catalytic oxidation of methane from the exhaust gas is one of the major challenges considering the difficulty of activating C-H bonds in methane (Ciuparu et al., 2002). Among the catalysts developed for methane oxidation, noble metal catalysts particularly alumina supported palladium catalysts (Pd/Al₂O₃) have attracted much attention due to their high activity at low temperature and stability even near to 900°C (Cargnello et al., 2012; Chen et al., 2015; Duan et al., 2019; Gelin and Primet, 2002; He et al., 2020). For Pd/Al₂O₃ catalysts, PdO is commonly considered to be the most active phase for methane oxidation and is stable up to 800°C. Researchers have investigated the behavior of palladium in Pd/Al₂O₃ for methane oxidation, proposed that PdO was essential for the low-temperature activity (Burch et al., 1995; Chen et al., 2015; Fan et al., 2012; Matam et al., 2010; Roth et al., 2000; Zou et al., 2020). At high temperatures, PdO decompose into Pd, which can also catalyze the combustion of methane. Previous studies also revealed that the crystal phase of Al₂O₃ had a great influence on the activity and stability of Pd/Al₂O₃ by tuning metal-support interaction, and the reducibility and oxygen capacity of catalyst (Murata et al., 2017; Park et al., 2014). Alumina with θ -, δ -, κ -, η -, and γ phases were employed as supports for preparation of PdO/Al₂O₃, and it was found that the θ -Al₂O₃ supported one (PdO/ θ -Al₂O₃) exhibited the highest activity for methane oxidation due to the enhanced reducibility and the largest oxygen capacity (Park et al., 2014). However, it should be noted that, Pd catalysts often suffered a transient deactivation in cooling ramps, typically occurs from 800 to 500°C (Cargnello et al., 2012; Grunwaldt et al., 2007; Mihai et al., 2017; Monai et al., 2015). Such transient deactivation is related to the hysteresis of temperatures between PdO decomposition and Pd reoxidation, and the catalytic activity of metallic Pd is much lower compared with PdO within this temperature range (Grunwaldt et al., 2007; Matam et al., 2010; McCarty, 1995; van Vegten et al., 2009).

Nitrogen oxides (NO_x) always coexist in lean-burn NGV exhausts, and thus it is important to investigate the influence of NO_x on the catalytic oxidation of methane. Ocal et al. (2000) found that NO (2.3%) co-fed improved the catalytic activity of Pd/hexaaluminate catalyst for methane oxidation above 410°C, attributed to the increase of Pd reoxidation or the formation of reactive O* by NO₂ (from NO oxidation) dissociation. Similarly, Hurtado et al. (2004) proposed that a little amount of NO₂ (60 ppmV) could slightly increase the methane conversion over a Pd/Al₂O₃ catalyst. More recently, a positive effect of NO₂ and NO on the long term activity and prevented deactivation of the Pd-Pt/Al₂O₃ catalyst was observed by Gremminger et al. (2015).

As for catalytic methane oxidation, it should be noted that, numerous studies have focused on the influence of NO_x on light-off activity of the employed catalysts (Gremminger et al., 2015; Hurtado et al., 2004; Ocal et al., 2000). To the best of our knowledge, however, there is little information available in literature involving the influence of NO_x on the transient deac-

tivation of Pd/Al_2O_3 for methane oxidation. To highlight this issue, herein, NO (1000 ppmV) was introduced into the fed gas during the complete oxidation of methane over Pd/θ - Al_2O_3 catalyst. It was found that NO, as a co-exist component in simulated NGV exhaust, can alleviate the transient deactivation of Pd/θ - Al_2O_3 during the complete oxidation of methane. Further investigation shows that such alleviation of transient deactivation was mainly attributed to the formation of NO₂, the occurrence of which increased the content of more active PdO on the catalyst surface, befitting the methane oxidation over Pd/θ - Al_2O_3 catalyst. In addition, NO_x could participate in homogeneous reaction between CH₄, and O₂, thus might be partially contributed to the alleviation above 650°C.

1. Materials and methods

1.1. Catalyst preparation

The fresh 2 wt.% Pd/θ - Al_2O_3 catalyst was prepared by traditional impregnation method. Al_2O_3 support was obtained by calcining industrial pseudo boehmite (Shandong Aluminum Co. Ltd.) in air at 1050°C for 2 hr. The obtained Al_2O_3 was then suspended in deionized water with constant stirring for 30 min. Pd precursor solution, obtained by dissolving $Pd(NO_3)_2 \cdot 2H_2O$ (Aladdin) in deionized water, was then added to the alumina suspension drop by drop. The slurry was stirred at room temperature for 1 hr, and followed by evaporating at 60°C in a rotavapor. The obtained catalyst powder was then dried at 100°C overnight in an oven and calcined 2 hr at 600°C in air.

1.2. Catalyst characterization

Nitrogen adsorption-desorption isotherms at -196°C were obtained on a TriStar II 3020 apparatus (Micromeritics, USA). Prior to the experiment, the fresh catalyst was evacuated at 300°C for 6 hr. The total surface area of the sample was determined by the Brunauer-Emmett-Teller (BET) theory.

Thermogravimetric analysis (TGA) experiment was performed on a high temperature thermogravimetric analyzer (TGA/DSC1/1600, Mettler Toledo, Switzerland) in air atmosphere. The weight changes of fresh catalyst in the heating process from 200 to 1100°C with a ramp rate of 25°C/min and the natural cooling process were recorded.

The O₂ temperature programmed oxidation (O₂-TPO) experiment was conducted on a ChemStar chemisorption analyzer (Quantachrome, USA), a quadrupole mass spectrometer (HPR20, Hiden Analytical, UK) was also equipped to record the O₂ signal (mass/charge = 32). The fresh catalyst (80 mg) was heated from 200 to 900°C and then cooled to 200°C at the rate of 10°C/min in flowing 1 vol.% O₂/He of 30 mL/min, during which O₂ mass signal was recorded against temperature.

To reveal the actual information about the catalysts after reactions (used catalysts), the fresh catalysts were first pretreated in specific reaction conditions with or without the NO_2 co-fed similar with the activity tests will be mentioned latter (reaction treatment), then the reaction gases were cut off imTable 1 – Pretreatment of Pd/θ -Al₂O₃ catalysts for CO pulse chemisorption, scanning transmission electron microscopy (STEM), powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) characterizations.

	Reaction conditions		Protection conditions	
Catalyst	Ambient	Temperature	Ambient	Temperature
Fresh catalyst	-	-	Air	RT
Used catalyst 1	0.1 vol.% CH ₄ , 3.5 vol.% O ₂	200-900-200°C	N ₂	200°C-RT
Used catalyst 2	0.1 vol.% CH ₄ , 3.5 vol.% O ₂ , 200 ppmV NO ₂	200-900-200°C	N ₂	200°C-RT
Used catalyst 3	0.1 vol.% CH4, 3.5 vol.% O2	200-900-650°C (held for 90 min)	N ₂	650°C-RT
Used catalyst 4	0.1 vol.% CH ₄ , 3.5 vol.% O ₂ , 200 ppmV NO ₂	200-900-650°C (held for 90 min)	N ₂	650°C-RT
RT: room temperature	e.			

mediately and the catalysts were cooled down to room temperature (RT) only in the exposure of flowing N₂ (Chen et al., 2020) (protection treatment). All samples were collected and stored in a sample tube filled with N₂ for subsequent characterizations, with the detailed information list in Table 1. CO pulse chemisorption measurements of used catalysts were performed using ChemStar chemisorption analyzer (Quantachrome, USA). Approximately 80 mg samples were put into a sample tube and pretreated under 5 vol.% H₂/Ar at 60°C for 120 min and then under He at 250°C for 30 min. After the sample was cooled to 30°C in He, pulse chemisorption measurement was performed with 5 vol.% CO/He while monitoring the effluent with a thermal conductivity detector. Pd dispersion was calculated by assuming that CO was adsorbed on surface Pd at 1:1 (= Pd:CO) stoichiometry.

Palladium particle size distributions were obtained by scanning transmission electron microscopy (STEM, JEM 2100F, JEOL, Japan). The samples for STEM experiments were pretreated with the same procedures as the CO pulse chemisorption tests.

Powder X-ray diffraction (XRD) patterns of supports, fresh and used catalysts were determined by a diffractometer (D8 ADVANCE, Bruker, Germany) employing Cu K α radiation ($\lambda = 0.15418$ nm) within the 2 θ range of 5° to 90° with a step size of 0.02°.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a scanning X-ray microprobe (ES-CALAB250XI, Thermo Fisher Scientific, USA) using an Al $K\alpha$ excitation source (1486.6 eV). The binding energy (BE) was calibrated by using the C1s peak at 284.6 eV as standard. Before the XPS measurement, the samples were pretreated with the same procedures as the XRD experiments.

1.3. Activity measurement

The catalytic activity was tested in a fixed-bed quartz flow reactor. The catalyst particles sieved through 40–60 mesh were placed in the middle of a quartz tube. The total feed gas flow was held at 300 mL/min, with composition of 0.1 vol.% CH₄, 3.5 vol.% O₂ (1000 ppmV NO, or 200 ppmV NO₂ if co-fed), balanced by N₂. For catalyzed reactions, 100 mg catalyst particles were used, given the gas hourly space velocity (GHSV) of ~180,000 mL/(g•hr). For the uncatalyzed reaction, feed gas flow passed through the empty reactor. The inlet and outlet gas compositions were monitored using an Antaris IGS gas analyzer (Thermo Fisher Scientific, USA) equipped with a heated, low-volume multiple-path gas cell. The CH_4 conversion was calculated following Eq. (1):

$$CH_4 \text{ conversion} = \left(1 - \frac{[CH_4]_{out}}{[CH_4]_{in}}\right) \times 100\%$$
(1)

where, $[CH_4]_{out}$ (ppmV) and $[CH_4]_{in}$ (ppmV) are the outlet and inlet CH_4 concentrations, respectively.

Temperature program reactions were carried out with ramping from 200 to 900°C (heating step) at a rate of 5°C/min and then back to 200°C (cooling step). The catalyst was also tested with time on stream during the cooling step, the catalytic activity was measured for 5 hr at 650°C with and without NO_x co-fed.

2. Results and discussion

2.1. NO_x effect on transient deactivation

Fig. 1a shows the catalytic activity of 2 wt.% Pd/ θ -Al₂O₃ (surface area $87.5 \text{ m}^2/\text{g}$) for methane oxidation in the absence and presence of NO (1000 ppmV) with the ramps of heating and cooling. During heating step (solid lines), the Pd/ θ -Al₂O₃ catalyst achieved 50% methane conversion at around 314°C, reaching 100% at around 410°C and keeping complete methane oxidation even up to 900°C, which was close to the performance in previous reports (Table S1). Introduction of NO into the fed gas resulted in a higher light-off temperature for methane oxidation if compared with that in NO-free condition, indicative of activity decay induced by NO co-fed. During cooling step (dotted lines), whether NO existed or not, the catalyst suffered obvious transient deactivation. In the absence of NO, the loss of methane conversion was observed between 800 and 500°C with a maximum of around 35%. In the presence of 1000 ppmV NO, transient deactivation was observed between 700 and 550°C, with a maximum CH₄ conversion loss of around 23%. Obviously, it is interesting that NO co-fed results in different effects on methane oxidation, which is closely related to the reaction temperature. Specifically, the existence of NO could alleviate the transient deactivation of Pd/θ -Al₂O₃ for methane oxidation at high temperature range (above 500°C), while decreased the low-temperature activity (below 410°C) as a result of partial blocking of the active sites (Auvinen et al., 2020; Sadokhina et al., 2017). A second activity test was also carried out in reaction mixture with and without NO co-fed



Fig. 1 – Methane oxidation over Pd/θ - Al_2O_3 : (a) CH_4 conversion with and without NO co-fed; (b) NO_x concentration during methane oxidation with NO co-fed. Reaction conditions: 0.1 vol.% CH_4 , 3.5 vol.% O_2 , 1000 ppmV NO (if co-fed) and N_2 balance, 300 mL/min, gas hourly space velocity (GHSV) 180,000 mL/(g·hr).

(Fig. S1). The presence of 1000 ppmV NO again alleviated transient deactivation between 800 and 500°C, which confirmed the stability of Pd/θ -Al₂O₃ for methane oxidation. To reveal such temperature-dependence effect, meanwhile, NO_x concentrations were also measured during methane oxidation in the presence of NO, with results shown in Fig. 1b. As for heating process, it is interesting that the formation of NO2 was observed at around 380°C. With reaction temperature increasing, the concentration of NO2 increased, reaching the maximum of 180 ppmV at 460°C, and then decreased gradually. Within this temperature range, an opposite tendency was observed for NO concentration. At a given temperature, it should be noted that the total amount of NO and NO₂ was close to the inlet NO concentration (1000 ppmV), indicating the occurrence of NO oxidation to NO2. This result in turn, indicated that selective catalytic reduction by methane (CH₄-SCR) did not occur in the lean condition. In other words, the transient deactivation may not be alleviated by CH₄-SCR reaction. During the cooling step, the direction oxidation of NO was observed between 750 and 350°C, within the temperature range of which the transient deactivation for methane oxidation occurred. Clearly, the presence of NO₂ alleviates the transient deactivation of Pd/ θ -Al₂O₃ for methane oxidation. At low temperature range (below 400°C for heating process and below 350°C for cooling step), NO₂ was hardly observed, during which methane conversion decreased if NO was co-fed. In other words, the presence of NO₂ promoted methane oxidation over Pd/θ -Al₂O₃ while the presence of NO resulted in an activity loss of the catalyst. The direction oxidation of NO over Pd catalyst in the absence and presence of CH₄ was also measured, with the conversion shown in Fig. S2. The results indicated that Pd/θ -Al₂O₃ was active for in situ formation of NO₂ above 250°C, which could alleviate the transient deactivation in methane oxidation. As a result, the following experiments and discussion will focus on the situation of co-fed of NO2, and compared with that one in NO₂ free conditions.

To illustrate the influence of NO_2 on methane oxidation, catalytic activity of Pd/θ - Al_2O_3 was further investigated with and without the co-fed of NO_2 . As shown in Fig. 2a, in the presence of 200 ppmV NO_2 , transient deactivation was observed when the temperature was reduced from 700 to 550°C. The

maximum of CH_4 conversion loss is around 12%, much smaller than the one observed with 1000 ppmV NO co-fed (23%). This result clearly showed that the co-fed of NO₂ could significantly alleviate the transient deactivation of the catalyst especially at around 650°C. At low temperature range, it should be noted that the introduction of NO₂ also decreased methane oxidation, which is similar with that of co-fed of NO.

NO_x concentrations were also measured during methane oxidation in the presence of NO₂, with results shown in Fig. 2b. It should be noted that the reverse reaction of NO oxidation easily occurred at temperature between 200 and 300°C, resulting in almost disappearance of NO₂ at the temperature of 300°C. At this temperature, meanwhile, methane conversion in heating process was below 10%. As a result, a suppression effect by NO₂ co-fed is reasonable considering that NO₂ was hardly observed within the light-off range of 300-400°C for methane oxidation. At temperature above 400°C, NO₂ appeared, giving the maximum concentration at 460°C for heating step, and at 420°C in cooling process, which was similar to that in NO co-fed. Taking this into account, therefore, it is reasonable that co-fed of NO2 could alleviate the transient deactivation of Pd/ θ -Al₂O₃ especially at around 650°C. In the whole temperature range, the total outlet concentration of NO_x was about 200 ppmV, being close to the inlet NO₂ concentration, which again, indicated that the NO oxidation and its reverse reaction occurred. Considering that the practical condition of catalyst includes water, activity measurements with and without NO2 were repeated two times in the presence of 14 vol.% H₂O (Fig. S3). In both cycle tests, the phenomenon that the NO2 alleviated transient deactivation still exits.

Torkashvand et al. (2019) reported that NO_x in lean-burn exhaust could participate in the homogeneous oxidation of methane and promote methane conversion. To illustrate the possibility of NO_x homogeneous reaction in alleviating transient deactivation, uncatalyzed reaction was carried out in an empty reactor (Fig. 3). In the absence of NO_2 , methane was not consumed during the whole test ramps. By comparison, the existence of 200 ppmV NO_2 greatly promoted the oxidation of methane at temperatures above 650°C. This result indicates that homogeneous reaction may partially alleviate transient



Fig. 2 – Methane oxidation over Pd/θ - Al_2O_3 : (a) CH₄ conversion with and without NO₂ co-fed; (b) NO_x concentration during methane oxidation with NO₂ co-fed. Reaction conditions: 0.1 vol.% CH₄, 3.5 vol.% O₂, 200 ppmV NO₂ (if co-fed) and N₂ balance, 300 mL/min, GHSV 180,000 mL/(g·hr).



Fig. 3 – Methane conversion in empty reactor with and without NO₂ co-fed. Reaction conditions: 0.1 vol.% CH₄, 3.5 vol.% O₂, 200 ppmV NO₂ (if co-fed) and N₂ balance, 300 mL/min, GHSV 180,000 mL/(g•hr).

deactivation above 650°C. As for alleviation between 650 and 500°C, homogeneous reaction can be neglected.

In order to further study the alleviating mechanism of NO₂ on transient deactivation at 650°C, isothermal experiments were conducted. Methane conversion was recorded with time on stream in the heating and cooling ramps, with and without NO₂ (200 ppmV) co-fed. The results in Fig. 4a showed that when the temperature was reduced and kept at 650°C, methane conversion in the absence of NO2 increased from 60% to 70% within the initial 0.5 hr, and then almost maintained in the next 4.5 hr. Compared with that without NO₂ cofed, a faster and more significant increase in methane conversion took place with the co-existence of NO₂, increasing from 70% to 90% in the initial 0.5 hr. To highlight such alleviation of NO2 on transient deactivation, the isothermal experiment was carried out by varying gas composition at 650°C, with results shown in Fig. 4b. In the first isothermal period of 2 hr, the catalyst was exposed to the mixture of CH₄, O₂ and N₂, being similar as shown in Fig. 4a. In this period, the methane conversion increased from 60% to 70% and then almost maintained, also

being in agreement with the results of Fig. 4a. Once 200 ppmV NO₂ was added in the feed gas, methane conversion increased obviously and then kept at 80%. When NO₂ was cut off, the activity decreased back to the level of the first 2 hr. This behavior demonstrated that NO₂ can improve methane oxidation over the Pd/ θ -Al₂O₃ at 650°C, and such improvement is reversible.

2.2. Change of Pd species in the heating and cooling step

The hysteresis of temperatures between PdO decomposition in the heating process and Pd reoxidation in the cooling process is regarded as the key factor on the transient deactivation (Grunwaldt et al., 2007; Matam et al., 2010; McCarty, 1995; van Vegten et al., 2009). The TGA and the O₂-TPO experiments, therefore, were performed to confirm the change of Pd species in the heating and cooling cycle. As shown in Fig. 5, the weight loss occurred between 200 and 750°C was likely due to the evaporation of adsorbed water and surface hydroxyls of catalyst (Datye et al., 2000), while the weight loss above 750°C was resulted from the PdO decomposition to Pd and the weight lose rapidly. In the cooling from 1100 to 700°C, the weight was not changed, indicating that the metallic Pd derived from the PdO decomposition in the heating stage has not been re-oxidized. Further cooling from 700 to 650°C, the weight of the catalyst picked up sharply, attributing to the Pd re-oxidation. O2-TPO experiment was also performed to investigate the change of Pd species, and the results were shown in Fig. 6. During the heating process, a positive peak in O₂ mass signal was observed at around 730°C, belong to the decomposition of PdO to Pd. During cooling, a negative peak in O₂ signal was observed at around 440°C, corresponding to the uptake of O_2 by Pd to form PdO.

2.3. Relationship between the Pd state and the transient deactivation

Considering that the activity of catalyst can be affected by Pd dispersion (or Pd size), the change of which is related to the reaction atmosphere and temperature (Demoulin et al., 2005; Murata et al., 2017). With this in mind, the Pd sizes after the activity tests with and without NO₂ existence were determined.



Fig. 4 – Methane conversion over Pd/θ-Al₂O₃ as function of time on stream (a) with and without NO₂ co-fed; (b) with NO₂ added in and cut off. Reaction conditions: 0.1 vol.% CH₄, 3.5 vol.% O₂, 200 ppmV NO₂ (if co-fed) and N₂ balance, 300 mL/min, GHSV 180,000 mL/(g•hr).



Fig. 5 – Thermo-gravimetric pattern of fresh catalyst with consecutive heating (at the rate of 25°C/min) to 1100°C and cooling to 200°C.



Fig. 6 – O₂ temperature programmed oxidation profiles of fresh catalyst. Inlet gas: 1 vol.% O₂/He with consecutive heating and cooling at the rate of 10°C/min.

CO pulse chemisorption measurement and STEM were performed over the used catalysts 3 and 4. Pd dispersion was calculated from total adsorption gases, with results list in Table 2. Palladium particle size distributions were obtained by observation using STEM, and the size distribution histograms were shown in Fig. 7. Compared with the used catalyst 3, the used catalyst 4, undergoing the same heating-cooling cycle with NO₂ co-fed, exhibited similar Pd dispersion and size. As a result, the alleviation effect of NO₂ was not related to the change of Pd size.

To further reveal the effect of NO₂ on the state of Pd, aluminum support, fresh and used catalysts (Table 1) were characterized by XRD, with the results shown in Fig. 8. The XRD patterns confirmed that the catalyst support was θ -Al₂O₃ (Murata et al., 2017; Park et al., 2014). The fresh Pd/θ -Al₂O₃ catalyst shows major and significant peaks at $2\theta = 33.8^{\circ}$ and 42.0° corresponding to PdO, while the peaks assigned to Pd metal $(2\theta = 40.1^{\circ}, 46.8^{\circ} \text{ and } 82.1^{\circ})$ (Honkanen et al., 2017; Lee et al., 2020; Murata et al., 2017; Park et al., 2014) are almost not observed. After exposed to $CH_4 + O_2$ (used catalyst 1) and to $CH_4 + O_2 + NO_2$ (used catalyst 2) with reactions heating from 200 to 900°C and then cooling back to 200°C (being similar to the heating-cooling cycle in Fig. 2), the feature patterns of PdO were also observed, while exhibited much higher intensity if compared with the fresh catalyst. It means that PdO particle size increases after the methane oxidation with above mentioned process, no matter NO₂ exists or not. This is consistent with the reports of Demoulin et al. (2005) and Briot and Primet (1991), who observed the increasing of palladium particles size after methane oxidation.

After the exposure of $CH_4 + O_2$ with reaction heating from 200 to 900°C and then cooling to 650°C for 90 min (denoted as used catalyst 3, being similar to the heating-cooling cycle in Fig. 4), Pd metal patterns were observed with a strong intensity, indicating that the PdO continuously decomposed into Pd metal during isothermal reaction at 650°C. Meanwhile, no PdO pattern was observed, which would be due to two following reasons: first, all of PdO over the catalyst decomposed into Pd metal; second, the content of PdO was too low to detect. Compared with the used catalyst 3, the used catalyst 4, undergoing the same heating-cooling cycle while NO₂ was co-fed into CH₄ + O₂, exhibited the similar XRD patterns each other.

Table 2 – Pd dispersions and particle sizes of catalysts.						
	CO pulse measurement		STEM			
Catalyst	Particle size (nm) ^a	Dispersion (%)	Particle size (nm) $^{\rm b}$			
Used catalyst 3	13.0	8.6	17.1±5.2			
Used catalyst 4	13.2	8.5	17.5±6.0			

^a Calculated from Pd dispersion assuming spherical Pd particles. ^b Calculated from size distribution presented in Fig. 7.





The chemical state of surface Pd of the fresh and used Pd/θ -Al₂O₃ catalysts was characterized by XPS, with Pd 3d spectra shown in Fig. 9. The central binding energies (BE) of Pd $3d_{5/2}$ peaks are marked in the figure. For the fresh sample and used catalysts 1 and 2 (Fig. 9a), the peaks at around 336.4 and 339.2 eV are ascribed to Pd²⁺ $3d_{5/2}$ and Pd⁴⁺ $3d_{5/2}$ respectively (Stefanov et al., 2015). Although Pd⁴⁺ (PdO₂) is highly unstable, it can exist as the outermost layer of surface PdO as a result of Pd exposure to air for a long time (Kibis et al., 2012). According to XPS results in Fig. 9a, the fresh catalyst and used catalysts 1 and 2 mainly contain oxidized Pd on the surface. This is consistent with the results of XRD, TGA, and O₂-TPO, indicating

that palladium of the catalyst was in oxidized state after the cooling reaction from 900 to 200°C.

For the used catalysts 3 and 4 (Fig. 9b), the two peaks at around 334.9 and 336.5 eV are ascribed to $Pd^0 3d_{5/2}$ and $Pd^{2+} 3d_{5/2}$ respectively (Gabasch et al., 2007; Gao et al., 2008; Li et al., 2020; Stefanov et al., 2015). The appearance of Pd metal confirms the decomposition of PdO after high temperature reaction (up to 900°C) and is consistent with the results of XRD, TGA, and O₂-TPO. The ratios of $Pd^{2+}/(Pd^0+Pd^{2+})$ (calculated by peak area) for the used catalysts 3 and 4 are 20% and 25%, respectively, the latter of which shows a higher proportion of Pd^{2+} . Compared with the XRD results above, an un-



Fig. 8 – Powder X-ray diffraction patterns of support and catalysts.

expected finding is that larger amount of Pd²⁺ species exist on the catalyst surface when NO₂ is co-fed in the isothermal reaction. It has been reported in literatures (Ocal et al., 2000; Smirnov et al., 2018; Wickham et al., 1991; Zheng and Altman, 2000) that NO₂ adsorbed and dissociated into NO and O* over the Pd-based catalysts, and the O* oxidized the metallic Pd to Pd²⁺, the occurrence of which promoted the formation of more active Pd²⁺ sites. On the basis of the above catalytic activity results, it is easy to find the two-fold influence of NO on the activity of Pd/θ -Al₂O₃ catalyst for methane oxidation: under the heating process, the existence of NO inhibited methane oxidation in the light-off temperature range of 200-410°C; meanwhile, under the cooling process, the presence of NO alleviated the transient deactivation occurred at high temperature. The inhibition of NO on the low temperature activity, relating to the block of activity sites, was reported by the previous studies (Auvinen et al., 2020; Sadokhina et al., 2017). The alleviation of NO on the transient deactivation in the temperature range of 800–500°C, while has not been reported yet.

During the alleviation in the cooling ramp, an in situ formation of NO₂ was observed, which promoted methane oxidation over Pd/θ -Al₂O₃ while the presence of NO resulted in an activity loss. As reported in the literatures (Burch et al., 1995; Matam et al., 2010; Roth et al., 2000), PdO is commonly considered to be the most active phase for methane oxidation below 800°C. With this in mind, it could be speculated that the presence of NO₂ might change the chemical state of Pd, and then affect the activity of CH_4 oxidation over the Pd/θ - Al_2O_3 catalyst. Comparing the XRD and XPS results of the used catalysts 1 and 2 (in Figs. 8 and 9), however, the presence of NO₂ had no effect on the crystal structure and the valence state of Pd after the heating-cooling test. Looking back at the Table 1, the treatment temperatures of the used catalysts 1 and 2 both went from 200 to 900°C, and then down to 200°C, leading to the possibility that the changes of Pd state occurred in the transient deactivation (800–500°C) were not detected by XRD and XPS. Thus, we analyzed the Pd state of the used catalysts 3 and 4 after the exposure of $CH_4 + O_2$ with reaction heating from 200 to 900°C and then cooling to 650°C for 90 min. Surprisingly, the results of XPS indicate that the co-fed of NO₂ favors the formation of Pd²⁺ species, exhibiting the much better catalytic activity for CH₄ oxidation in the temperature range of 800–500°C occurred the transient deactivation.

In a word, the presence of NO₂ favoured the formation of more active Pd^{2+} species on Pd/θ -Al₂O₃ catalyst, and thus reasonably alleviated the transient deactivation. Glancing at Fig. 3, one can easily find that the homogeneous reaction between CH₄, O₂ and NO_x may be partially responsible for the alleviation (above 650°C).

3. Conclusions

To conclude, in this study, the influence of NO_x on Pd/ θ -Al₂O₃ catalyst was investigated by conducting heating-cooling cycle tests (between 200 and 900°C) and isothermal tests (at 650°C) in lean-burn methane oxidation. Pd/ θ -Al₂O₃ catalyst suffered transient deactivation in the cooling ramp from 800 to 500°C, resulting from the hysteresis between PdO decompo-



Fig. 9 – X-ray photoelectron spectroscopy patterns (Pd 3d) of catalysts. (a) From top to bottom: fresh catalyst, used catalyst 1, used catalyst 2. (b) From top to bottom: used catalyst 3, used catalyst 4.

sition and Pd reoxidation confirmed by TGA, O₂-TPO. NO cofed inhibited the methane oxidation in low temperature (below 410°C), whereas, alleviated the transient deactivation in the temperature range of 800-500°C. More than that, the in situ formation of NO₂ favoured the formation of active PdO particles on Pd/ θ -Al₂O₃ catalyst, and thus reasonably alleviated the transient deactivation. Homogeneous reaction between CH₄, O₂ and NO_x might be partially responsible for the alleviation above 650°C.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2021.04.020.

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